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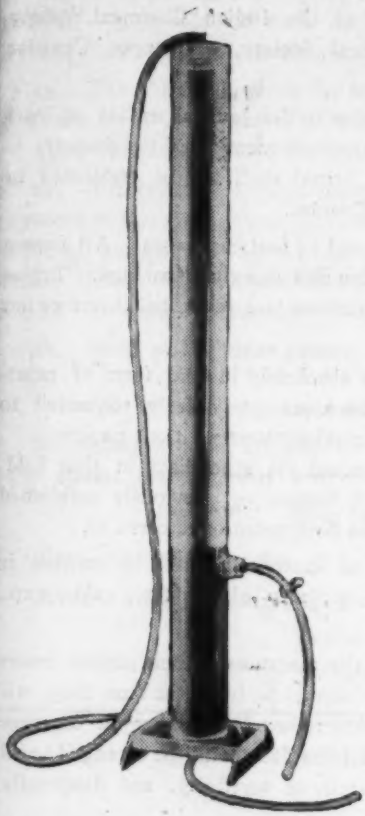

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ON THE STUDY OF THE USE OF CALCIUM OXALATE MONOHYDRATE IN THE INVESTIGATION OF RARE EARTH AND THORIUM ACTIVITIES

By B. C. Purkayastha and S. N. Bhattacharyya

It has been shown that $CaC_2O_4.H_2O$ is a faithful carrier of rare-earth and thorium activities. The distribution of activities under the experimental conditions has all along been found uniform. Calcium is therefore a good non-isotopic diluent for the study of thorium and rare-earth activities as oxalates. The fact that calcium oxalate carries cent per cent rare-earth and UX_1 activity, has been utilised to prepare carrier-free UX_1 from aged uranyl nitrate solution with about cent per cent recovery. It can be claimed to be a very convenient method for determining counter geometry factor. It has been shown that calcium can be estimated within a very short time with aged uranyl nitrate solution where UX_1 acts as a radioactive indicator. In time of measurements, the soft β^-'s from UX_1 are cut off and the hard β^-'s from UX_2 in equilibrium are actually counted. This is very convenient, because changes due to resultant effect of absorption and scattering over a wide range of source weight are negligibly small. So no correction factor is required. It has been shown that rare earths can be uprooted from uranium, thorium, zirconium, beryllium and aluminium to the desired level by calcium oxalate ($CaC_2O_4.H_2O$) as scavenger. In this work the ratio of rare earths to uranium etc. elements (mentioned above) has been brought to about $1:10^8$. It has been found to be a very simple laboratory process of decontamination.

There is no simplified method for the determination of rare-earth and UX_1 activities by isotopic dilution. Previously the rare-earth and thorium activities in question were diluted by lanthanum and thorium respectively and precipitated as oxalate, and this was ignited to oxide which was then transferred to counting tray for activity measurements in the solid way. In case of rare earths, it is time consuming and is handicapped by other factors, well known to workers in the field. Besides the difficulties mentioned, the activities from the thorium series also play a disturbing role in case of weak activities. In view of these difficulties American investigators (Coryell and Sugarman, "Radiochemical Studies: The Fission Product", Book-3, 1951, p. 1681) tried to find out a condition to treat rare-earth and thorium oxalates as primary standards. But the conditions they found out were not also very convenient and faithful in the studies lasting for a few days with solid samples. Difficulties with thorium, as mentioned with special reference to radioactive contaminants, remain unanswered. One of the objectives of our investigation is to find out a non-isotopic diluent which yields a faithful primary standard and at the same time which can carry all the thorium and rare-earth activities along with it and that the conditions can be made such that a uniform distribution is achieved through the entire mass of the precipitate so as to enable a fraction to be used as in the usual practice of isotopic dilution.

It has further been observed that various methods have been described in the literature (Crookes, *Proc. Roy. Soc.*, 1900, **66**, 409; Booth, *J. Chem. Ed.*, 1951, **28**, 144; Erbacher, *Z. anorg. Chem.*, 1944, **252**, 282; Aten and Barendregt, *Physica*, 1950, **16**, 760; Wahl and Bonner, "Radioactivity Applied to Chemistry", 1951, p. 431) for the

separation of UX_1 in equilibrium with U_1. No simple method has thus far been successful to separate cent per cent UX_1 containing no carrier ion in it. The second objective of this investigation is to find out a non-isotopic carrier which carries UX_1 from U_1, but the objective UX_1 ion and the carrier in question can be easily separated from each other. In this type of separation procedure, the carrier for UX_1 should be chosen such that it should carry the ultramicro quantity of thorium (UX_1) leaving the bulk of U_1 behind it and at the same time it is better if the carrier in question should not have a tendency of complex formation so that any simple chemical or physico-chemical procedure can be applied without much complexity for uprooting a few atoms of thorium (UX_1), leaving behind the bulk of carrier employed. Selection naturally comes to calcium because of the following advantages: (*a*) Calcium has got very little tendency to form complex ion. (*b*) Oxalates and fluorides of calcium are insoluble in acetic acid and it has been found by us that calcium oxalate in acetic acid medium carries about cent per cent thorium, and the conditions may be made such that calcium oxalate may be perfectly freed from uranium too. In the present investigation calcium oxalate has been used as a carrier of UX_1 and a method of separating UX_1 freed from any carrier has been described.

It has been further observed that for various types of nuclear studies, decontamination of trace of rare earths from elements like uranium, thorium, zirconium, aluminium and beryllium is indispensable. It also forms a part of the study whether trace of rare-earth oxalates can be carried along with calcium oxalate, leaving behind the elements in question as double oxalates. Although various methods of decontamination have been described in the literature of nuclear science, such a simple procedure as studied by us has been found to be very suitable for simple laboratory work. With these objects in view, a study on the use of calcium oxalate monohydrate was undertaken.

Experimental

Reagents used were all of Analar quality. A stock solution of uranyl nitrate in nitric acid was prepared. It was filtered through sintered glass crucible and allowed to remain as such for about six months before quantitative investigation started. Carrier-free Pm^{147} and Y^{91}, which were used in the present investigation, were supplied by Harwell, England, as chloride in hydrochloric acid solution.

Role of Calcium Oxalate Monohydrate in the Determination of Rare-earth and Thorium (UX_1) *Activities.*—To test the suitability of the use of calcium as a good isotopic diluent for thorium and rare earths, unknown calcium was determined by using UX_1, Pm^{147} and Y^{91}. The procedure consists in coprecipitating the thorium and rare-earth activities along with $CaC_2O_4.H_2O$. The latter was precipitated in acetic acid medium by the addition of oxalic acid. It was observed that some calcium remained in the solution. This difficulty was later overcome by precipitating calcium from 50% alcoholic solution. The description of a typical experiment is given below.

A known amount of the active solution is taken to which is added a known amount of $CaCl_2$ solution. Free mineral acid is neutralised with ammonia using methyl red as indicator and then acidified with acetic acid. The solution is next diluted to about 65 c.c. and heated to boiling. To the hot solution are added 75 c.c. of absolute alcohol

and 10 c.c. of oxalic acid (containing about 1g. of $C_2H_2O_4.2H_2O$) all at once with constant stirring. This is allowed to stand for sometime when the precipitate readily settles. The precipitate is washed by centrifugation, slurried with acetone, transferred to a nickel tray and dried under an infra-red lamp, taking care that the temperature does not exceed 105°. The precipitate on the tray is weighed as $CaC_2O_4.H_2O$ and counted in the usual way. Unknown calcium is then determined by comparing with a known standard.

TABLE I

Estimation of calcium using UX_1, Pm^{147} and Y^{91} *as indicating nuclei.*

Indicating nuclide.	Amount of calcium taken.	Amount of calcium found.	Indicating nuclide.	Amount of calcium taken.	Amount of calcium found.	Indicating nuclide.	Amount of calcium taken.	Amount of calcium found.
Pm^{147}	22.7 mg.	23.1±0.6 mg.	Pm^{147}	46.5 mg.	46.5±0.9 mg.	Y^{91}	28.4mg.	29.0±0.6 mg.
Pm^{147}	19.9	19.9±0.5	UX_1	22.7	22.6±1.3	Y^{91}	34.1	33.9±0.7
Pm^{147}	23.3	23.6±0.4	UX_1	26.1	26.8±1.5	Y^{91}	39.8	39.7±0.9
Pm^{147}	34.9	34.8±0.7	UX_1	19.3	19.0±1.0	Y^{91}	45.4	46.1±1.1
			Y^{91}	11.4	11.4±0.2			

Direct Use of Aged Uranyl Nitrate Solution in the Determination of Calcium by Iotopic Dilution.—In our previous operations we separated UX_1 from aged uranyl nitrate solution. It has also been observed by us that aged uranyl nitrate solution as such can conveniently be used as a source of UX_1 in the determination of calcium by the principle of isotopic dilution. A known amount of an aged uranyl nitrate solution was added to the solution of the unknown calcium and precipitation of $CaC_2O_4.H_2O$ was done in the way as already described. The precipitate was washed through centrifugation and a fraction of the precipitate was taken for counting. Unknown calcium can thus be easily estimated. Results are indicated in Table II.

TABLE II*

Estimation of calcium using aged uranyl nitrate solution itself as a source of UX_1.

Ca taken (mg.) ...	11.4	14.2	17.0	22.7	28.4	36.9
Ca found (mg.) ...	11.2±0.4	13.9±0.4	16.5±0.6	22.9±0.8	27.8±0.8	37.3±1.0

*Uranium taken in each case = 0.13371 g. Volume of operation = ~150 c.c.

$CaC_2O_4.H_2O$ *as an Intermediary for the Preparation of Carrier-free* UX_1.—As the separation of calcium and thorium can be easily achieved, $CaC_2O_4.H_2O$ can suitably be employed for the preparation of carrier-free UX_1 in quantitative yield (vide Table III). Our present method consists of the following three simple steps:

1. Carrying of UX_1 in equilibrium with U_1 with $CaC_2O_4.H_2O$.

2. Isolation of UX_1 from calcium through $Fe(OH)_3$ scavenger.

3. Separation of iron by continuous extraction with *iso*propyl ether. The aqueous layer which is obtained consists of cent per cent UX_1 in hydrochloric acid, free from any carrier. That the recovery is cent per cent has been studied by the following procedure.

The solution of uranyl salt after uprooting UX_1 with $CaC_2O_4.H_2O$ was tested for the completeness of separation by precipitating a fresh quantity of $CaC_2O_4.H_2O$. No appreciable activity was detected, indicating that carrying of UX_1 by $CaC_2O_4.H_2O$ was cent per cent. The procedure was followed in all the steps mentioned above. We also tested the activity carried in the following way to have a duplicate check. Standard sample was prepared from known amounts of uranium and calcium. This was treated as a standard for comparison with the carrier-free product. In case of the same amount of uranium, identical activity within statistical error was always observed, both from liquid samples and solid samples as $CaC_2O_4.H_2O$. This evidently proves that $CaC_2O_4.H_2O$ is a faithful carrier and the procedure adopted is perfectly reliable. Further evidence to the findings mentioned above and suitability of our procedure for measuring counter geometry was given by evaporating an aliquot portion of the solution of carrier-free UX_1 on a thin mica foil and counting through a delimiting diaphragm (Cook and Duncan, "Modern Radiochemical Practice", 1952, p. 267). After making necessary corrections, the observed number of counts was found to agree well with that calculated theoretically within the limits of statistical accuracy (Table III).

TABLE III*

Testing the recovery of carrier-free UX_1 and the suitability of the method for determining counter geometry.

No.	Counting from solid samples.		Counting from liquid samples.		Counting through delimiting diaphragm.	
	No. of counts per min. recorded from		No. of counts per min. recorded from		No. of disintegrations per min.	
	Standard.†	Final recovery product.	Standard.†	Final recovery product.	Theoretical	Exptl.
1.	4590	4645	3006	3002	329600	339800
	±122	±145	±49	±49		±13060
2.	4590	4380	3006	2910	329600	339800
	±122	±123	±49	±49		±10370

* Both the experiments were started from 0.4457 g. of uranium to prepare carrier-free UX_1.
† Standard samples were prepared as described in the experimental portion.

Role of $CaC_2O_4.H_2O$ *in the Decontamination of Rare-earths from Materials commonly used in Atomic research such as* U, Th, Zr, Be, Al, *etc.*—In order to study whether calcium oxalate by repeated precipitation could uproot rare earths from the materials mentioned above, these were converted into double oxalate by excess of ammonium oxalate to which were added 0.247 mg. of lanthanum and a known amount of Pm^{147} as a rare-earth indicator. Successive calcium oxalate precipitations were then made. Results are shown in Table IV.

TABLE IV†

Use of $CaC_2O_4.H_2O$ *in decontaminating rare earths from* Be, Al, Zr, Th *and* U.

Major constituent (M).	Initial ratio. M : R.	M : R in soln. after precipitation with $CaC_2O_4.H_2O$. 1st. pptn.	2nd. pptn.	*3rd. pptn.
Be	$1 : 2.47\times10^{-3}$	$1 : 1.4\times10^{-5}$	$1 : 1.8\times10^{-7}$	$1 : 8.6\times10^{-9}$
Al	$1 : 2.47\times10^{-3}$	$1 : 8.8\times10^{-6}$	$1 : 5.2\times10^{-7}$	$1 : 2.6\times10^{-8}$
Zr	$1 : 2.47\times10^{-3}$	$1 : 8.1\times10^{-6}$	$1 : 5.3\times10^{-7}$	$1 : 3.3\times10^{-8}$
Th	$1 : 2.47\times10^{-3}$	$1 : 2.6\times10^{-5}$	$1 : 1.2\times10^{-6}$	$1 : 4.4\times10^{-8}$
U	$1 : 2.47\times10^{-3}$	$1 : 1.3\times10^{-5}$	$1 : 5.3\times10^{-7}$	$1 : 2.1\times10^{-9}$

† M stands for the major constitutent such as Be, Al, Zr, Th and U; R stands for rare earth. Initial concentration of M in all cases is about 100 mg. and that of R is 0.247 mg. of lanthanum per 100 c.c. of the solution. 104 mg. of $CaC_2O_4.H_2O$ was precipitated in each case.

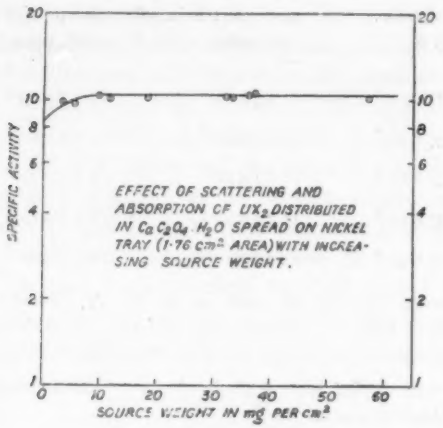
* Rare-earth activity was carried here with lanthanum oxalate except in the case of thorium where it was carried with thorium oxalate itself.

DISCUSSION

The method to use calcium as a non-isotopic diluent for the measurement of rare-earth and thorium activities by percipitating as calcium oxalate is free from the troubles already mentioned. That $CaC_2O_4.H_2O$ spreads well and furnishes very reliable results is evident from our studies on the determination of calcium using UX_1 (thorium isotope), Pm^{147} (representative of the rare earths), Y^{91} (a representative of the chemical analogue of the heavy rare earths). The method can be claimed very reliable and free from complexities. When from the tracer scale we go to increase the rare earth or thorium content, the method, as is usual, does not succeed, presumably because of the complex oxalato-ion formation. It has been observed by us that the maximum inactive carriers, which we can have in all these cases, are about 0.5 mg. each of yttrium, thorium and lanthanum (in case of Pm). When we go beyond this limit of 0.5 mg. carrier per 150 c.c. of the solution, error creeps in due to incomplete carrying. This limitation does not, however, stand in our way in distribution and other radiochemical studies with tracer amount of thorium and rare-earth activities. Besides, use of calcium is very convenient when we deal with long lived rare-earth activities which are costly to procure, because when the study is over we can easily separate the active constituent once again by the easy chemical procedure. It should further be stated that in the case of UX_1, the soft β^-'s from the isotope in question were cut off by 35.3 mg./cm^2 of aluminium absorber. So we measured the hard β^-'s from the short-lived UX_2 in equilibrium with its mother. It is well known that absorption and scattering correction in case of hard β^-'s for a source weight is very negligible over a wide range of source weights (Coryell and Sugarman, "Radiochemical Studies: the Fission Products," Book-1, 1951, p. 56) for comparative studies, and in this respect it is a very convenient isotope where correction in the estimation by isotopic dilution

is not required (vide Fig. 1). In this respect UX_1 or Y^{91} can conveniently be used even in the estimation of calcium by isotopic dilution in simple cases. It should be

FIG. 1



mentioned that in the case of Ca^{45} we meet with soft β^-'s where changes in self-absorption and self-scattering against changes in source weight are very predominant and some error is prone to follow. It should further be stated that in our measurements we have estimated different quantities of unknown calcium, keeping rather the activity the same, which is evidently the same as measuring the differing quantities of unknown activities. It is also an evidence that the distribution of the activities over the $CaC_2O_4.H_2O$ is very uniform over a wide range. Any fraction of the $CaC_2O_4.H_2O$ taken, as is usually done, is a measure of the total activity. The cause of this uniform distribution of thorium and rare-earth activities over $CaC_2O_4.H_2O$ is a subject matter of further study.

The fact that unknown calcium can conveniently be estimated by using a known amount of aged uranyl nitrate solution as a source of UX_1 (vide Table II) is much easier than the classical method in consideration of the simplicity and the time of operation. Even the amount of uranium used up can be used again as soon as the amount of UX_1 sufficiently grows up.

It must be pointed out that carrying of cent per cent UX_1 or rare-earth activities by $CaC_2O_4.H_2O$ offers a very great advantage. We have utilised it, besides the purpose mentioned above, to have carrier-free UX_1 in solution so that by dropping an aliquot portion on a thin mica foil we can determine the counter geometry. The procedure followed by us is not, however, very simple. There are other ways wherein it is possible to recover cent per cent UX_1 directly from calcium and that will form the subject matter of a separate study.

In our study of decontaminating rare earths from elements such as beryllium, aluminium, zirconium, uranium and thorium, the solution eft after three successive calcium oxalate precipitations was acidified with hydrochloric acid and any trace of

rare-earth activities was tested by carrying as lanthanum oxalate, whilst the final degree of decontamination achieved in case of thorium was tested by precipitating thorium oxalate itself. The results showing the degree of decontamination achieved in different stages are shown in Table IV. Simplicity of operation allures one to adopt it to uproot rare earths in day-to-day laboratory work. Even in case of analysis dealing with small traces of rare earths, calcium oxalate can serve as a good scavenging agent.

From the facts stated above it can be claimed that calcium oxalate monohydrate is a very useful carrier for rare-earth and thorium activities in the field of study already mentioned. Other uses of this reagent will form the subject matter of further study.

The authors express their deep sense of gratitude to late Prof. M. N. Saha for his encouragement in the work. They are thankful to Prof. B. D. Nag for his keen interest in the work of this division.

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THE FRIEDEL-CRAFTS REACTION OF NAPHTHALENE WITH BENZENE- AND *p*-TOLUENE-SULPHONYL CHLORIDE

By V. Baliah and Mrs. Aleykutty Mathew

The Friedel-Crafts reaction of naphthalene with benzene- and *p*-toluene-sulphonyl chloride has been studied in the presence of different catalysts (aluminium, stannic, ferric and zinc chlorides) and different solvents (nitrobenzene, methylene chloride, ethylene chloride and carbon tetrachloride). The product generally is a mixture of the α- and β-naphthylsulphones. The ratio of the isomers varies with experimental conditions. The optimum temperature for the reaction varies with the catalyst and solvent. The α-substitution is greater below 100°, but negligible above 200°.

Naphthalene usually affords a mixture of α- and β- isomers in substitution reactions. The ratio of the two isomers can be considerably varied by altering the experimental conditions. The Friedel-Crafts acylations are reported to be influenced more by the nature of the reagent and solvent than by the temperature (Gore, *Chem. Rev.*, 1955, **55**, 242). Where the reagent is bulky, the entropy of activation for α-substitution will be considerably reduced, facilitating β-substitution. The solvent effect is more difficult to understand. It can be due to the solvent solvating or forming complexes with the reagents or transition states. Thus, the need for more experimental data to understand the solvent and steric effects is obvious.

The Friedel-Crafts reactions of naphthalene with arene-sulphonyl chlorides has not been well investigated (vide Beckurts and Otto, *Ber.*, 1878, **11**, 2066 ; Chrustschoff, *Ber*, 1874, **7**, 1167 ; Huismann, D.R.P. 701954/1941). The results of these workers, however, indicate that the catalyst used can control orientation. Hence, it appeared to be of interest to make a detailed study of this reaction, using different solvents.

Benzene- and *p*-toluene-sulphonyl chlorides were used for the investigation. The catalysts employed were aluminium chloride, stannic chloride, ferric chloride and zinc chloride. The solvent influence was studied with nitrobenzene, carbon tetrachloride, methylene chloride and ethylene chloride. In almost all cases the reaction furnished a mixture of the isomeric α- and β-naphthylsulphones, though the ratio of the isomers varied considerably with experimental conditions. The ratio of the isomers in each mixture was determined from the melting point—composition curve. The compositions, thus arrived at, were checked spectrophotometrically in many cases. Table I summarises the results obtained.

In the absence of a solvent the temperature, most suitable for each catalyst, was as follows : $AlCl_3$, 100-10° ; $FeCl_3$, 100-10° ; $SnCl_4$, 130-40° ; $ZnCl_2$, 200-10°. Higher temperatures generally led to the formation of a black material. At lower tenperatures the reaction was slow. With the data, thus obtained at different temperatures, it is not possible to correlate the yield with the catalyst. For example, the higher yields obtained with stannic chloride and zinc chloride cannot be ascribed to the greater efficiency of the catalyst, since in both cases higher temperatures were also employed.

The mixtures obtained with catalysts other than zinc chloride contained more of the α-isomer. The product with zinc chloride was mostly the β-isomer (95%). This is in accordance with the well-known fact that higher temperatures favour β-substitution. Even in the case of the Friedel-Crafts acylation of naphthalene, increased yields of the β-isomer were obtained at higher temperatures (Roux, *Ann. chim.*, 1887, *vi*, **12**, 289; Claus and Tersteegen, *J. prakt. Chem.*, 1890, **42**, 517; Caille, *Compt. rend.*, 1911, **153**, 393; Baddeley, *J. Chem. Soc.*, 1949, S101).

The influence of solvent was studied with nitrobenzene, methylene chloride, ethylene chloride and carbon tetrachloride, using aluminium chloride as catalyst in each case. Here again, certain difficulties were encountered to collect data under comparable conditions. For example, the reaction did not occur in nitrobenzene to any appreciable extent at low temperatures. With the other solvents, higher temperatures led to dark products which could not be purified.

The results obtained with methylene chloride, ethylene chloride and carbon tetrachloride offer a more interesting study. Here the data are comparable, the experimental conditions being identical. At a given temperature the yield does not seem to depend much on the solvent. With increase of temperature the yield is also raised. The products obtained in these solvents contain chiefly the α-isomer, the one obtained in ethylene chloride being exclusively the α-isomer. Here again, the higher content of the α-isomer cannot be wholly ascribed to the solvent. The temperature seems to have a greater control over the α : β ratio. The solvent effect, even if it exists, does not seem to be significant. A thorough analysis of all the results seems to reveal that the arene-sulphonyl chlorides react with naphthalene primarily at the α-position below 100°, the β-position being increasingly favoured above 100°. The α-substitution is negligible above 200°.

TABLE I

The Friedel-Crafts reaction of arene-sulphonyl chlorides with naphthalene.

Catalyst.	Solvent.	Temp.	Yield.	M.P. of the product.	Ratio of α- and β- isomers by M.P. method.	Ratio of α- and β- isomers by Spectrophotometric method.
		A. With benzenesulphonyl chloride.				
$AlCl_3$	None	100-10°	68%	80-82°	65 : 35	65 : 35
$SnCl_4$	,,	130-40°	75	82-85°	69 : 31	70 : 30
$FeCl_3$	,,	100-10°	64	78-82°	52 : 48	53 : 47
$ZnCl_2$	,,	200°	85	114-15°	5 : 95	3 : 97
$AlCl_3$	$PhNO_2$	140-60°	86	112-14°	7 : 93	...
$SnCl_4$	,,	,,	56	108-12°	10 : 90	...
$FeCl_3$	,,	130-40°	73	104-106°	17 : 83	...
$AlCl_3$	CH_2Cl_2	30°	20	93-95°	91 : 9	93 : 7
,,	$C_2H_4Cl_2$	,,	25	99-101°	100 : 0	100 : 0
,,	CCl_4	,,	18	90-92°	83 : 17	...

TABLE I (contd.)

Catalyst.	Solvent.	Temp.	Yield.	M.P. of the product	Ratio of α- and β- isomers by M.P. method.	Ratio of α- and β- isomers by Spectrophotometric method.
		B. with *p*-toluenesulphonyl chloride.				
$AlCl_3$	None	100-10°	59%	109-10°	65:35	64:36
$SnCl_4$	,,	130-40°	76	102-106°	76:24	73:27
$FeCl_3$	,,	100-10°	62	107-108°	82:18	85:15
$ZnCl_2$	,,	200°	89	159-60°	4:96	3:97
$AlCl_3$	$PhNO_2$	140-60°	86	145-50°	15:85	...
$SnCl_4$	,,	,,	64	144-47°	17:83	...
$FeCl_3$	,,	130-40°	67	152-55°	10:90	...
$AlCl_3$	CH_2Cl_2	45°	58	100-102°	71:29	66:34
,,	$C_2H_4Cl_2$	,,	60	119-20°	100:0	100:0
,,	CCl_4	,,	63	107-108°	81:19	87:13

EXPERIMENTAL

Analysis of Mixtures of α- and β-Naphthylsulphones.—The ratio of the α- and β-isomers in each mixture was determined from the melting point-composition curve. Synthetic mixtures of the pure isomers were prepared and their m. p. determined. These mixtures did not generally have a sharp m.p. but melted through a range. The point at which almost a clear liquid resulted was taken as the m.p. of the mixture. The variation of the m.p. with composition for the mixtures of α- and β-naphthylphenylsulphones and α- and β-naphthyl-*p*-tolylsulphones is given below.

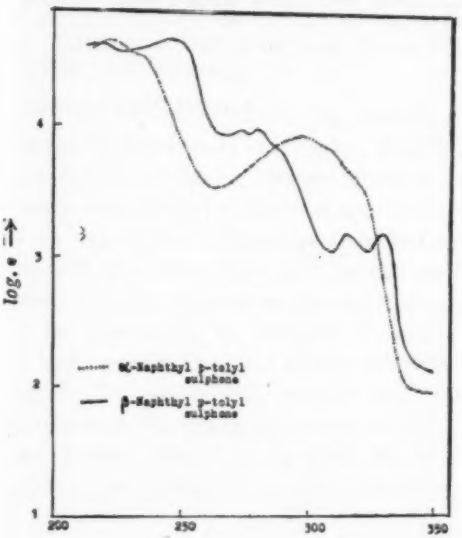
TABLE II

	α- & β-Naphthylphenylsulphones.						α- & β-Naphthyl-*p*-tolylsulphones.					
α (%)	100	90	80	70	60	55	100	90	80	70	60	50
M.P.	100°	95°	89°	84°	79°	78°	120°	114°	107°	101°	105°	114°
β (%)	100	90	80	70	60	50	100	90	80	70	60	
M.P.	117.5°	110°	103°	96°	89°	81°	163.5°	153°	144°	134°	123°	

These data were used to analyse sulphone mixtures obtained. In cases where the m.p. indicated two possible compositions, small amounts of pure α- and β-isomers were added separately to the mixture and the m.p. redetermined. If a mixture is richer in α-isomer, its m.p. will be raised by small additions of α-sulphone and depressed by small additions of β-sulphone.

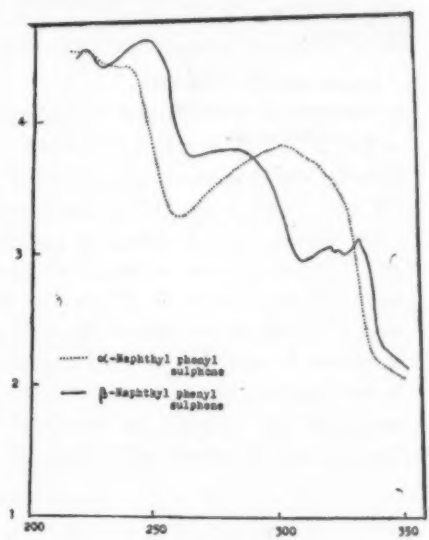
The quantitative estimation of the components of a mixture by the spectrophotometric method depends upon the fact that the total extinction of any mixture is a summation of the separate extinctions of the components (Gillam and Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold, London, 1954, p. 185). The absorption curves of α- and β-naphthylphenylsulphones (Fig. 2) and also those of α- and β-naphthyl-*p*-tolylsulphones (Fig. 1) were plotted and the compositions of the mixtures were determined by finding the extinction at suitable wave-lengths.

FIG. 1



Wave-length (mμ).

FIG 2



Wave-length (mμ).

General Procedure for the Friedel-Crafts Reaction.—A mixture of naphthalene (0.1 *M*), benzene- or *p*-toluene-sulphonyl chloride (0.1 *M*) and the catalyst (0.15 *M*) was heated to and kept at the required temperature (see Table I) for 30-40 minutes. The product was cooled and decomposed with HCl (dil.). The mixture of α- and β-naphthylsulphones, thus obtained, was recrystallised from ethanol. The α : β ratio was then determined.

When the reaction was carried out in various solvents, the amounts of solvents used and the duration of the reaction (given in parentheses) were as follows : nitrobenzene, 75 c.c. (30 minutes) ; methylene chloride, ethylene chloride or carbon tetrachloride, 200 c.c. (2 hrs. in the case of *p*-toluenesulphonyl chloride and 15 hours in the case of benzenesulphonyl chloride).

Preparation of Sulphones.—α-Naphthylphenylsulphone was prepared by the permanganate oxidation of α-naphthylphenyl sulphide. The latter was prepared from thiophenol and α-bromonaphthalene by the Mauthner method.

β-Naphthylphenylsulphone was similarly prepared starting from β-thionaphthol and iodobenzene.

Similar procedures were adopted for the preparation of the *p*-tolylsulphones. β-Naphthyl-*p*-tolylsulphone melted at 163-64°. Hans Meyer (*Annalen*, 1923, **433**, 327), who prepared it by passing the vapours of toluene over β-naphthalenesulphonic acid at 150°, reports m.p. 154°.

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, Model DU. The solvent used was 95% ethanol, purified by distillation after treatment with lead acetate and sodium hydroxide.

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ANODIC PHENOMENA IN THE ELECTROLYSIS OF LEAD FORMATE

By A. N. Kappanna and A. S. Dewagan

A study of the reactions at gold and platinum anodes in the electrolysis of lead formate solutions has been made. At low current densities up to 15 ma/cm^2, the only product at the anode is lead peroxide. At higher current densities, the peroxide formation is suppressed to some extent and carbon dioxide liberation also takes place. The presence of free formic acid lowers the current efficiency of the deposition of lead peroxide on the anode. Mechanisms have been suggested to account for the different anodic phenomena.

The earliest work on the electrolysis of aqueous lead formate solutions appears to be that of Warwick (*Chem. News*, 1892, **66**, 275). Warwick's idea was to get a cathodic deposit of lead. Electrodeposition of lead from formate solutions was studied more extensively by Mathers and Cockrum (*Trans. Amer. Electrochem. Soc.*, 1914, **26**, 117). In neither of these investigations do we have any reference to the anodic reactions in the electrolysis of this salt except where lead anodes were employed. The study of anode reactions in the electrolysis of lead formate is of interest in the light of an observation by Luckow (*Z. anal. Chem.*, 1869, **24**, 8) that the anodic deposition of lead peroxide from lead nitrate solutions is suppressed by the presence of reducing agents like oxalic acid, tartaric acid etc., and also in the context and continuation of previous studies in this laboratory on the anodic oxidation of formate ion (Kappana and Deoras, this *Journal*, 1951, **28**, 287 ; 1953, **30**, 345). The results of such a study are reported in the present communication.

Experimental

Lead formate was prepared by the dissolution of lead carbonate in formic acid and crystallised from the solution. Purification of the salt was effected by recrystallisation. A stock solution of the salt was prepared by saturation. The concentration of the solution was determined by the estimation of lead in the solution.

The electrolysis was effected in a 400 c.c. beaker using either platinum or gold electrodes. Potential measurements were all made with a precision potentiometer, and where necessary, a saturated calomel element was used as the reference electrode. Current efficiency measurements were made with the aid of a silver coulometer in the circuit.

Table I

Discharge and decomposition potentials.

The lead formate solution used had a concentration corresponding to 0.073 *M*.

Electrodes.	Anode discharge potential.	Cathode discharge potential.	Decomp. potential.
Platinum	1.03 volts	0.01 volt	1.04 volts
Gold	1.30	0.01	1.31

The anode and cathode current potential curves are quite smooth and normal and do not reveal any abnormalities in the phenomena at the electrodes

Cathodic Reaction.—Deposition of lead commenced almost immediately after the current was switched on even at low current densities, as is to be expected from the low cathode discharge potential. The deposits were in all cases flaky and not adherent. The current efficiency was found to be nearly 100%.

Anodic Reaction: Platinum Electrodes.—The colour of the anodic deposit varied slightly with current density. At low current densities it was reddish brown and deepened towards dark brown with increase in current density. The composition of the deposit was ascertained by analysing it both for its lead content and available oxygen. In all cases the deposit proved to be entirely lead dioxide. The difference in density of colour is obviously due to the difference in grain size.

There was no gas evolution at the anode up to a current density of 15 ma. Above this current density, there was gas evolution as well as deposition of lead dioxide. Anodic gases collected at different current densities proved to consist of CO_2 and small quantities of oxygen.

Gold Electrodes.—The results with gold electrodes were slightly different. Even at low current densities (5 ma) gas evolution was visible, but even so, the deposition of lead dioxide went on smoothly, though not exclusively. These results are summarised in Table II.

TABLE II

Area of electrode = 6 cm².

	Electrolyte.	Current density.	Duration of electrolysis.	Wt. of anodic deposit.
		Platinum electrodes.		
(1)	0.073 *M* lead formate	10 ma	30 mins.	0.132 g.
(2)	0.059 *M* ,, ,,	5	30	0.0596
(3)	,, ,, ,,	5	60	0.119
(4)	,, ,, ,,	10	30	0 120
(5)	,, ,, ,,	10	60	0.238
(6)	,, ,, ,,	15	30	0.182
(7)	Do + 0.1 *M*-Na formate	10	30	0.123
(8)	Do + 0.2 *M* ,,	10	30	0 1198
(9)	Do + *N*-formic acid	10	30	0.043
		Gold electrodes.		
(10)	0.073 *M* lead formate	5	60	0.0814 g.
(11)	,, ,, ,,	10	60	0.0832
(12)	,, ,, ,,	15	60	1.048

It will be observed that the amount of deposit on platinum electrodes in the first six results in Table II is very nearly proportional to the amount of current passed (up to a current density of 15 ma) irrespective of the concentration of the lead salt or the presence of neutral sodium formate.

Result (9) in the table is representative of the effect of formic acid in lowering the current efficiency in the deposition of lead dioxide. The result is interesting in so far as it shows that while the presence of formate ion (as by the addition of sodium formate) does not diminish the deposition of the oxide, free formic acid does. This is indicative of the more readily anodic oxidisability of free formic acid (undissociated) than the formate ion through the agency of plumbic ion. It cannot be argued that this is due to the presence of hydrogen ions, as it is well known that the quantitative anodic deposition of lead is effected in the presence of a large excess of free nitric acid. This observation appears to be contrary to the conclusion arrived at by Hammick *et al.* (*J. Chem. Soc.*, 1925, 2715 ; 1926, 1105) that the reactant in the homogeneous oxidation of formate by bromine and iodine is the formate ion and not free formic acid. In the present case, however, we are dealing with a heterogeneous reaction on the surface of an electrode. The reaction probably is

$$Pb^{4+} + HCOOH \longrightarrow 2H^+ + Pb^{2+} + CO_2.$$

Here again, the anodic gases collected proved to be almost entirely CO_2 (with small amounts of oxygen).

At current densities higher than 15 ma/cm^2 therefore, the presence of lead in solution exerts a more powerful oxidising influence in the anodic oxidation of formate ion, as there is no liberation of CO at all, as found with only alkali formates. This may mean that the formate radicals liberated on the anode react either (1) according to the equation

$$2HCOO \longrightarrow HCOOH + CO_2$$

or (2) they are oxidised by plumbic ion in accordance with the equation :

$$2HCOO + Pb^{4+} \rightarrow 2H^+ + 2CO_2 + Pb^{2+}.$$

Current Efficiency of Lead Dioxide Deposition.—Taking the average of the results of (1) to (8) in Table II, calculations show that 2.17 faradays of electricity are needed for the deposition of one molecule of PbO_2. This is rough reckoning with milliammeter readings. By calculating on the basis of silver deposited in the voltameter included in the circuit, the current efficiency has been found to be in the neighbourhood of 99%.

The current-potential curves have been found to be normal and no breaks occur on the curves right up to very high current densities. This is indicative of the uniformity of the discharge phenomena on the electrodes. The normal primary process on the anode is the discharge of formate ions, yielding formate radicals. The secondary processes following are probably in accordance with the following scheme :

$$Pb^{2+} + 2HCOO \longrightarrow Pb^{4+} + 2HCOO^-$$

The net electrolytic process could therefore be summed up as :

1. $Pb^{2+} + 2\ominus \longrightarrow Pb$ at cathode.
2. $2HCOO^- \longrightarrow 2HCOO + 2\ominus$ at the anode.
3. $2HCOO + Pb^{2+} \longrightarrow Pb^{4+} + 2HCOO^-$
4. $Pb^{4+} + 2H_2O \longrightarrow PbO_2 + 4H^+$ } on the anode

$$2Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + Pb$$

The formation of CO_2 at higher current densities has already been accounted for above. The reason why this should happen above a particular current density is to be understood as due to the increased surface concentration of discharged formate radicals and the possibility of surface catalysis on certain active centres in particular ways. The relative rates of the different surface reactions determine also which should predominate over the rest under different conditions.

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HYDROCHLORIC ACID SOLUTIONS CONTAINING SILICA. PART I. CONDUCTIVITY AND TRANSPORT NUMBER MEASUREMENTS

By Hussein Sadek and Sasson Abouharoun

The conductance of acidified solutions containing low-molecular silica, having the same equivalent amount of alkali and the same amount of HCl, has been examined as a function of the silica concentration. As the silica content increases, the conductance drops accordingly. The effect is considered as being due to adsorption of ions. This view has been supported by transport number experiments which prove that silica acts as a non-electrolyte and that the transport number of the chloride ion in these solutions is lower by about 5% than the corresponding solutions, void of silica.

Lösenbeck (*Koll.-Chem. Beih.*, 1922, **16**, 27) and Grundmann (*ibid.*, 1923, **18**, 197) studied the reactions of silicic acid sols with acids in a quantitative manner by measuring the conductivity of mixtures of silicic acid and HCl, and the mobility of the colloid by transport number experiments. They found the conductivity of the mixture to be considerably smaller than the sum of the conductivities of both the components. Silicic acid, when added to HCl, lowers its conductivity below that of HCl alone. The lowering is greater, the higher the concentration of silica. The isoelectric point of the sol was found to lie at 0.001 *N*-HCl for a sol containing 0.099% SiO_2. If the reactions taking place down to the isoelectric point only involve the suppression of the ionisation of silicic acid, the decrease in the conductivity at the isoelectric point must be equal to the original conductivity of the sol. It amounts, however, to a multiple of this value. Lösenbeck conceives the combination with HCl in such a manner that the silica particles behave as a sponge which becomes gradually filled with HCl, the hydrogen ions being expelled with a certain solution pressure.

Moreover, Pauli and Valko (*Kolloid Z.*, 1926, **38**, 289) studied the effect of addition of HCl to a well-defined sol, purified by electrodialysis. They showed that when the acid concentration was very low, the change in conductivity due to the binding was a time process. They assumed that after the isoelectric point had been overstepped, the silicic acid was undissociated. The decrease in the conductivity was explained as being due to the removal of HCl from solution in the form of the compound (SiO_2, HCl) through the formation of a basic chloride (SiO_2 H^+) Cl^-.

The aim of the present paper is to examine the binding process in the early stages of the ageing of the acid solutions containing low-molecular silica. The solutions were prepared by the addition of sodium silicate solution to hydrochloric acid while stirring (Sadek, this *Journal*, 1952, **29**, 507).

Experimental

Sodium silicate solutions were prepared in such a manner as to contain the same equivalent of NaOH and varying amounts of silica. The ratios of Na_2O : SiO_2 in the silicate solutions were 1 : 1, 1 : 1.5, 1 : 2, 1 : 2.33. These solutions have been designated as silicate solution I, II, III and IV respectively. Pure silica was obtained by the disintegration of commercial water glass with HCl (conc.). The gel formed was washed repeatedly with distilled water till the chloride ion test was negative. The product

was then dried in an oven at 115° for several days. The dry silica was ground in an agate mortar to obtain a uniform powder. It was then analysed for its water content and impurities in the usual manner. The silica obtained was 89.55% pure. An exactly 0.100*N*-HCl solution was prepared from the constant boiling acid.

Conductance Measurements.—The resistance of acidified sodium silicate solutions was measured according to the classical method of the Wheatstone bridge. An audio-frequency oscillator producing 1000 cycles was used. The resistance readings were obtained for several fillings of the cell and were found to vary within 0.2%. The cell constant was 4.4288, as determined by potassium chloride using the data of Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1411).

Transport Number Experiments.—An apparatus similar to that used by Lottermoser and Fritche (*Kolloid Z.*, 1937, **80**, 166) was employed. All parts of the apparatus were made of pyrex glass tubing of uniform bore, the inner diameter of which was 1.5 cm. A diagram of the apparatus is shown in Fig. 1. The anode compartment A is separated from the middle portion by a large stop-cock, T, having the same bore as the apparatus. The anode consisted of an amalgamated cadmium rod. The cathode, C, consisted of a pipe-form tube which was filled with pure mercury and covered with few crystals of copper sulphate. The capacity of the apparatus was 200 c.c. The total quantity of electricity was measured by means of a silver coulometer containing 20% silver nitrate solution. The apparatus was checked before use by filling it with 0.05 *N*-KCl solution. The transport number of the Cl^- ion was found to be 0.497 at 25°. This value is in good agreement with 0.501, found by Lottermoser and Fritche (*loc. cit.*) and with 0.490 found by Shemilt Davies and Gordon (*J. Chem. Phys*, 1948, **16**, 342).

FIG. 1

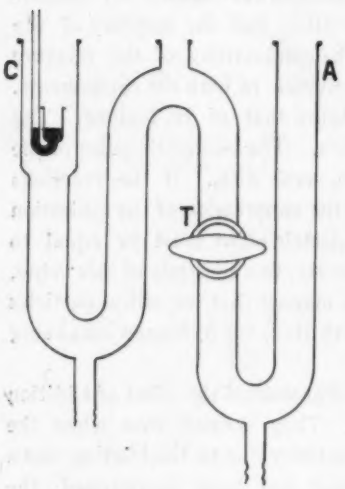


TABLE I

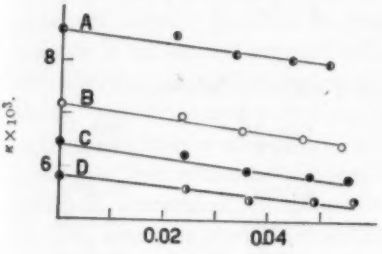
Soln.		NaOH +HCl.	Soln. I. +HCl.	Soln. II +HCl.	Soln. III +HCl.	Soln. IV +HCl.
A	moles SiO_2/litre	0.000	0.0221	0.0333	0.0443	0.0514
	1000 κ	8 570	8 476	8.141	8.067	7 950
B	moles SiO_2/litre	0.000	0.0233	0.0351	0.0466	0 0541
	1000 κ	7.190	6.974	6.680	6 542	6.474
C	moles SiO_2/litre	0.000	0.0240	0.0359	0.0480	0.0554
	1000 κ	6.470	6.237	5.944	5 859	5.805
D	moles SiO_2/litre	0.000	0.0245	0.0368	0.0490	0.0567
	1000 κ	5.812	5.578	5.375	5 401	5.408

Solutions A, B, C and D were obtained by mixing exactly 20, 22, 23 and 24 c.c. of 0.1*N*-alkali respectively to 25 c.c. of 0.1*N*-HCl and the solution diluted to 50 c.c. in a standard measuring flask.

DISCUSSION

Table I and Fig. 2 show the change of conductance of four sets of solutions each of which contains the same equivalent of alkali and the same amount of HCl. It can be readily seen that as the silica content increases, the conductance drops linearly. The curves run almost parallel to each other. The gradual drop in the conductance as the concentration of low-molecular silica increases could be explained on the basis of adsorption of conducting ions from solution. When these solutions were diluted, the conductance approached that of the corresponding acidified sodium hydroxide because of the break of the surface-adsorption complex. These findings indicate the surface combination of HCl with silica and confirm earlier conclusions (Sadek, *loc. cit.*).

FIG. 2



In order to elucidate the nature of the binding process, a comparison of the transport number of the Cl^- ion in these solutions with that in the corresponding acidified sodium hydroxide was carried out. The solutions were electrolysed for about 90 minutes. The results of a typical experiment on acidified sodium hydroxide is given below.

Original solution: 25 c.c. weighed 24.9926 g. and contained 0.03463 g. HCl, 0.06971 g. NaCl and 24.9194 g. H_2O.

Ag weighing 0.1383 g. was deposited corresponding to 0.04548 g. Cl^- ion forming 0.1176 g. $CdCl_2$.

Anode solution: All anode solutions weighed 55.4879 g. and contained 0.00283 g. HCl, 0.1299 g. NaCl, 0.1176 g. $CdCl_2$ and 55.2376 g. H_2O.

H_2O weighing 55.2376 g. should contain originally 0.1009 g. Cl^- ion. Cl^- ion migrating = 0.1270 − 0.1009 = 0.0261 ; hence

$$n_{Cl^-} = \frac{0.0261}{0.04548} = 0.587.$$

Table II shows the results obtained with acidified sodium silicate solutions. It can be readily seen that silica does not move in the electric current behaving, thus, as a non-electrolyte. This result is expected if one bears in mind that silicic acid is a weak acid of the same strength as HCN or boric acid ($pK_1 = 9.7$).

The effect of non-electrolytes, such as sucrose, on the conductance and p_H value in aqueous HCl solutions was investigated by Zhukov and Dneprov (*J. Gen. Chem. USSR.*, 1940, **10**, 291). They found that the transport number of the Cl^- ion remained constant in solutions containing sucrose up to 30% by weight. Similar experiments by Fisher and Koval (*Univ. Kiev Bull. Sci. rec. chim.*, 1939, **4**, 137) showed that sucrose, acetone and urea reduced the transport number of the H^+ ion in aqueous sulphuric

acid solutions. These findings are not in agreement with those of Erdey-Gruz (*Z. physikal. Chem.*, 1927, **131**, 87) who found that the addition of 7.1% mannitol increased the transport number of the H^+ ion in HCl solutions in the concentration range 0.01 – 0.10 *N*. Also Harned and Dreby (*J. Amer. Chem. Soc.*, 1939, **61**, 3113) observed an increase in the transport number of the H^+ ion in aqueous HCl solutions containing dioxane up to 20%.

TABLE II

Transport number of the Cl^- ion in acidified silicate solutions.

Original solution:	Soln. I +HCl.	Soln. II +HCl.	Soln. III +HCl	Soln. IV +HCl.
Wt. of 25 c c	24.9707	24.9744	25.0105	24.9965
Cl^- ion	0.04594	0.04610	0.04580	0.04584
HCl	0.00427	0.00525	0.00569	0.00558
NaCl	0.0689	0.06757	0.0664	0.0667
SiO_2	0.0358	0.0526	0.0651	0.0820
H_2O	24.8617	24.8490	24.8733	24.8422
Middle solution:				
Wt. of 25 c.c.	24.9721	24.9704	24.9967	24.9913
Cl^- ion	0.0460	0.0460	0.0458	0.0460
SiO_2	0.0360	0.0525	0.0649	0.0822
Ag deposited	0.1391	0.1460	0.1300	0.1304
Anode solution:				
Wt. of 25 c.c.	25.0191	25.0088	25.0123	25.0878
Cl^- ion	0.0534	0.0544	0.0545	0.0545
SiO_2	0.0355	0.0525	0.0647	0.0828
Anode soln.	73.8784	65.4618	68.3191	70.4956
HCl	0.0165	0.0106	0.0207	0.0291
NaCl	0.1642	0.1458	0.1405	0.1355
$CdCl_2$	0.1182	0.1241	0.1104	0.1108
SiO_2	0.1061	0.1416	0.1767	0.2334
H_2O	73.325	65.0640	67.971	69.987
n_{Cl^-}	0.560	0.552	0.561	0.562

The results reported here indicate that the transport number of the Cl^- ion in the presence of 0.024 – 0.056 mole SiO_2/litre is lower by about 5% than the value obtained in the corresponding solution, void of silica. The decrease in the conductance of the solutions with increasing concentration of silica could therefore be due to the decrease in the mobility of the Cl^- ions. The consequent increase in the mobility of the H^+ ions does not outweigh the decrease in the mobility of the Cl^- ions since the latter are more abundant in the solution.

However, Benton and Elton (*Trans. Faraday Soc.*, 1953, **49**, 1213) showed that powdered silica dissolved in aqueous HCl solutions due to the formation of colloidal silica on the surface. The ξ-potential was found to amount to -90.5 mv. This result was obtained from conductivity measurements which indicated an increase upon the addition of silica. These results, although contradicting our findings, show that the process taking place with powdered silica is not necessarily the same as that with low-molecular silica. If silica is charged negatively in Benton and Elton's sense, it should migrate in the electric current, which is not the case. It seems quite probable that the dehydration of low-molecular silica in solution affects the adsorption energies of the H^+ and Cl^- ions in such a manner as to become equal. If this is true, low-molecular silica will adsorb H^+ as well as Cl^- ions with equal probability. This assumption lends itself to explain the fact that silica does not move in the electric current and that solutions containing low-molecular silica possess a lower conductance than the corresponding solutions of acidified sodium hydroxide.

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HYDROCHLORIC ACID SOLUTIONS CONTAINING SILICA. PART II. POTENTIOMETRIC MEASUREMENTS

BY HUSSEIN SADEK AND SASSON ABOUHAROUN

*p*Cl measurements with the help of the silver chloride electrode were carried out at 25° on solutions containing low-molecular silica in the concentration range of 0.02—0.056 mole per litre. The results indicate that adsorption is taking place in these solutions. An equation has been developed which fits in with the experimental data. p_H values run in a parallel manner.

In an earlier communication by one of us (Sadek, this *Journal*, 1952, **29**, 507) *p*Cl mearsurements on acidified sodium metasilicate solutions were reported. The results indicate a pronounced increase in *p*Cl values over those calculated on the assumption that the Cl^- ions are totally free but nearer to those calculated on the basis of combination of one mole HCl per mole SiO_2, and confirm the idea of compound formation between silica and HCl (Lösenbeck, *Koll.-Chem. Beih.*, 1922, **16**, 27; Tourky, *Z. anorg. Chem.*, 1939, **240**, 198). In Part I of this series (Sadek and Abouharoun, this *issue*, p. 443) it has been observed that silica behaves as a non-electrolyte and that adsorption of ions by low-molecular silica is responsible for the decrease on conductance and of the transport number of the Cl^- ion below the corresponding value in solutions, void of silica. If this view is correct, one should find an incease in p_H and *p*Cl values as the concentration of silica increases in the the solution. In this communication potentiometric

measurements of the H^+ and Cl^- ions have been made and the results confirm the idea of adsorption of these ions by freshly formed low-molecular silica.

EXPERIMENTAL

Preparation of alkali silicate solutions I, II, III and IV and of 0.1*N*-HCl was described in Part I (*loc. cit.*).

p_H measurements were carried out with the help of a Beckman p_H-meter (model H). The instrument was standardised before use by means of a potassium biphthalate buffer of p_H 4.

pCl measurements were determined with the help of the silver-silver chloride electrode, prepared according to MacInnes and Parker (*J. Amer. Chem. Soc.*, 1915, **37**, 1445). Several such electrodes were prepared and those which gave zero potential against each other, when immersed in dilute HCl solution, were chosen for the determination of the Cl^- ion activity. The selected electrodes were tested before use in the silica-containing solutions by immersion in HCl solutions of known activities. The data of Lewis and Randall ("Thermodynamics and the Free Energy of Chemical Substances", McGraw Hill, 1923, p. 336) were plotted on a large scale such that the mean activity of the prepared solutions could be easily interpolated. The HCl solutions were obtained from the constant boiling acid by weight dilution. Table I shows the behaviour of the best electrodes. The cell which was used could be represented as:

Hg, Hg_2Cl_2, sat. KCl//HCl soln., AgCl, Ag.

All potentiometric measurements were carried out in a thermostat adjusted at 25°.

TABLE I

The standard potential of the AgCl, Ag *electrode.*

m.	E cell.	E° AgCl, Ag.	m.	E cell.	E° AgCl, Ag.
0.11850	0.0473 v	0.2288 v	0.02370	0.0860 v	0.2272 v
0.05925	0.0652	0.2289	0.01185	0.1058	0.2294
0.04740	0.0700	0.2287	0.00593	0.1228	0.2287

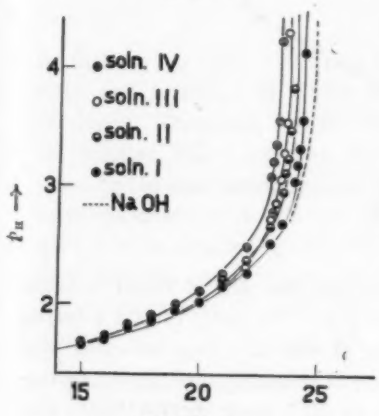
Mean : 0.2286 v

It can be seen that the average value of E° is about 6 mv higher than the accepted value. Lewis and Randall (*loc. cit.*) report 0.2234 v; Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 641) gave 0.2223 v, while Randall and Young (*ibid.*, 1928, **50**, 989) found 0.2221 v. The deviation is definitely due to the inclusion of a liquid junction potential across the saturated ammonium nitrate-agar salt bridge. According to Afanasiev (*ibid.*, 1930, **52**, 3477) silver chloride electrodes exhibit variation in the value of their standard potentials because of the lack of uniform method of electrode preparation; the various manipulatory conditions have a marked effect on the characteristics of the surfaces of silver halides and, hence, they have different potentials. Inspite of this discrepancy, the selected electrodes have been used since relative rather than absolute values are more important in the solutions containing silica.

Discussion

p_H Measurements.—Fig. 1 shows the titration curves of 25 c.c. of 0.1 *N*-HCl solution against various alkali silicate solutions containing increasing amounts of silica. It is quite remarkable to find that the curves do not coincide on each other, although these solutions are equinormal with respect to their sodium hydroxide content. The departure from the dotted curve for sodium hydroxide is therefore due to the interference of low-molecular silica. For a given quantity of alkali added, the p_H is higher, the higher the concentration of silica in the reagent. This result is in harmony with earlier findings that adsorption is prevailing in these solutions. The p_H increases as the H^+ ions are removed from solution by adsorption.

Fig. 1



One must bear in mind that low-molecular silica in these solutions behaves as a non-electrolyte formed by the suppression of ionisation of silicic acid in the presence of H^+ ions. The suppressed acid, as an ion-pair, would be expected to attract a number of water molecules around it on account of its high polarity (Sadek, this *Journal*, 1951, **28**, 619). This effect would affect the p_H in the opposite direction, thus causing a decrease (Sadek and Zayan, *ibid.*, 1953, **30**, 823). The above measurements indicate that in solutions near the end-point (above 85% neutralisation), the adsorption effect outweighs the solvation effect. This conclusion supports the early findings of the decrease in conductance as the concentration of silica increases.

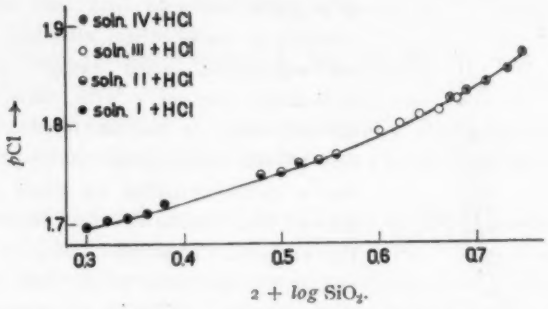
*p*Cl *Measurements.*—Equilibrium values were always obtained within 30 minutes from immersion of the silver-silver chloride electrode, and then they began to change with time. Table II shows the *p*Cl values obtained from several measurements on mixtures containing increasing amounts of silica and the same total concentration of Cl^- ions. These mixtures were prepared by adding, with constant stirring, varying aliquots of alkali silicate (solution I, II, III or IV) to 25 c.c. of 0.1 *N*-HCl and diluting the mixture to 50 c.c. in a standard volumetric flask. The mixtures denoted by the symbols A,B,C,D and E represent those made by the addition of 20,21,22,23 and 24 c.c. of alkali silicate respectively.

Table II

Mixture.	Soln. I+HCl.		Soln. II+HCl.		Soln. III+HCl		Soln. IV+HCl.	
	*p*Cl.	Mole SiO_2/l.	*p*Cl.	Mole SiO_2/l.	*p*Cl.	Mole SiO_2/l.	*p*Cl.	Mole SiO_2/l.
A	1.697	0.020	1.748	0.0300	1.792	0.040	1.826	0.047
B	1.704	0.021	1.751	0.0315	1.799	0.042	1.833	0.049
C	1.706	0.022	1.760	0.0330	1.811	0.044	1.843	0.0513
D	1.716	0.023	1.762	0.0345	1.815	0.046	1.857	0.054
E	1.721	0.024	1.768	0.0360	1.825	0.048	1.873	0.056

Fig. 2 shows a plot of pCl against $(2+\log SiO_2)$. The relation is quite linear at low concentration of silica and shows a more rapid increase at higher concentrations. It

FIG. 2



can also be seen that over the limited range of any one of the four sets a linear relation can be found as was shown previously (Sadek, *loc. cit*). In order to gain a deeper insight into the nature of these solutions, a calculation of the Cl^- ions adsorbed was made. For comparison several measurements of the pCl value obtained for the corresponding solutions prepared by the addition of NaOH to HCl were carried out. The average value was 1.633 ± 0.005. This corresponds to a chloride ion activity of 0.02328. Table III shows the amounts of Cl^- ions adsorbed per mole SiO_2.

TABLE III

Mixture.	$a_{Cl(obs.)}$.	$a_{Cl(ad.)}$.	$a_{Cl(ad.)}/SiO_2$.	$a_{Cl(obs.)}$.	$a_{Cl(ad.)}$.	$a_{Cl(ad)}/SiO_2$.
	Solution I+HCl.			Solution II+HCl.		
A	0.02009	0.00319	0.160	0.01786	0.00542	0.180
B	0.01977	0.00351	0.167	0.01774	0.00554	0.176
C	0.01968	0.00360	0.164	0.01738	0.00590	0.179
D	0.01950	0.00378	0.164	0.01730	0.00598	0.173
E	0.01901	0.00427	0.178	0.01706	0.00622	0.173
			Mean : 0.166			Mean : 0.176
	Solution III+HCl.			Solution IV+HCl.		
A	0.01614	0.00714	0.152	0.01493	0.00835	0.209
B	0.01589	0.00739	0.151	0.01461	0.00859	0.205
C	0.01545	0.00783	0.153	0.01435	0.00893	0.203
D	0.01531	0.00797	0.148	0.01390	0.00938	0.204
E	0.01496	0.00832	0.149	0.01340	0.00988	0.206
			Mean : 0.151			Mean : 0.205

It can be seen that the amount of Cl^- adsorbed per mole SiO_2 is almost constant, having an average value of 0.175.

If one assumes that the amount of Cl^- adsorbed {Cl(ad)} is proportional to the Cl^- ion concentration originally present {Cl(o)} and to the silica content, one can write the relation,

$$Cl(ad) = k\, Cl(o)\, (SiO_2)^n$$

also
$$Cl(free) = Cl(o) - Cl(ad)$$
$$= Cl(o)[1 - k(SiO_2)^n]$$

therefore
$$pCl = pCl(o) - \log [1 - k(SiO_2)^n].$$

Assuming that $k\,(SiO_2)^n < 1$, one gets

$$pCl = pCl(o) + k(SiO_2)^n.$$

By plotting $\log [pCl - pCl\,(o)]$ against $\log (SiO_2)$ a straight line was obtained from the slope and intercept of which the values of k and n were found to be 4.0 and 1.2 respectively. Therefore, over the range of silica concentration 0.02 – 0.056 mole per litre, the relation $pCl = 1.633 + 4\ (SiO_2)^{1.2}$ is valid. The derivation of the above relation is based on the assumption that the state of aggregation of low-molecular silica is the same in all the mixtures and that the activity coefficient is not influenced by the presence of silica. It is concluded that the presence of these discrete charges on the molecule of silica does not give it enough mobility to be detected analytically. Besides, these surface charges seem to be the initial stage in the coagulation process in Greenberg and Sinclair's sense (*J. Phys. Chem.*, 1955, **59**, 435).

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AMINO DERIVATIVES OF TITANIUM TETRABROMIDE. PART II

By Sarju Prasad and Jai Beniprasad Tripathi

Amino derivatives of titanium tetrabromide have been prepared by the action of titanic bromide on some aromatic secondary and tertiary amines, and their properties and structures studied.

The preparation and properties of the compounds formed by the action of titanic bromide on some aromatic primary amines have been studied in a previous communication (this *Journal*, 1956, **33**, 838), which shows that though the co-ordination number of titanium in these compounds is only four, but they are fairly stable. The work has been further extended to study the action of some aromatic secondary and tertiary amines on titanium tetrabromide under similar conditions.

Experimental

The amines used were of Merck's or B.D.H. 'extra pure' quality. Titanium tetrabromide was prepared by the method of Olsen and Ryan (*J. Amer. Chem. Soc.*, 1932, **54**, 2215), redistilled at 230° and extracted with ether which was distilled over metallic sodium.

General Method of Preparation.—In all the cases, except those mentioned below, the solution of amine in ether was added to the ethereal solution of titanic bromide with constant stirring. When the requisite quantity of the amine solution was added, a precipitate settled down. It was stirred well, kept for about an hour, filtered quickly and washed with ether till the washings did not give any precipitate with titanium tetrabromide. In the case of dimethylaniline and quinoline, the ethereal solution of titanic bromide was added to the amine solution in order to obtain a crystalline precipitate, as a pasty mass, which was not converted into a crystalline precipitate, was formed when the process of addition was reversed. The precipitate was dried over calcium chloride, analysed, and the properties of the compounds studied. Duplicate experiments were carried out in each case. The results reported in the tables are the average of of the two values.

Estimation.—Bromine was estimated by Piria and Schiff's method, nitrogen by the Dumas method and titanium as TiO_2. In all the compounds except tetraquinolino-titanic bromide, amine was also estimated by the potentiometric method and the percentage of nitrogen in the compound calculated. From Table I, the percentage of nitrogen obtained by this method appears to compare well with the results obtained by the Dumas method in all the compounds except tetradimethylanilino-titanic bromide, where a low value is obtained, due evidently to the hygroscopic nature of the compound.

Estimation of Amine by Potentiometric Method.—About 200-350 mg. of the compound was weighed out accurately, dissolved in alcohol and a few c.c. of H_2SO_4 (dil.) added to remove the slight turbidity due to hydrolysis of the compound, and the volume

made up to 100 c.c. A portion of the solution (10 c.c.) was pipetted out in a beaker and to it were added $2N$-H_2SO_4 (10 c.c.) and $M/2$-KBr. It was then titrated by $KBrO_3$ ($0.1N$) at the room temperature. When $KBrO_3$ was added to the solution, it was consumed and there was a gradual change in potential, but near the equivalence point a sudden jump in the potential due to a slight excess of the reagent (free bromine) was observed in all the cases.

As some of the amines examined formed dibromo and others, tribromo derivatives under similar conditions, a blank experiment was carried out in each case with the pure amine under identical conditions (only the graph for diphenylamine is shown: vide Fig. 1, curve IV).

The curves I, II, III and V in Fig. 1 and the curves VI-X in Fig. 2 refer to the estimation of the amine in tetra (-methyl-, -ethyl-, -benzyl)- anilino-, tetra-diphenylamino-, tetra (-dimethyl-, -diethyl-, -benzal-, -dibenzyl)-anilino-, and di-*p*-aminodiethylanilino-titanic bromide respectively

TABLE I

[T.B. denotes titanic bromide]

Compound.	Wt. of the compound.	Wt. of the amine Calc	Found (from the curves).	% Nitrogen.
Diphenylamine	0 2292 g.	0 2292 g.	0.2296 g.	8 30
Tetra-methylanilino-T.B.	0.2338	0.1257	0.1253	7.01
„ -ethylanilino-T.B.	0.2842	0.1614	0.1611	6.56
„ -benzylanilino-T.B.	0.3520	0.2342	0.2345	5.01
„ -diphenylamino-T.B.	0.3006	0.1946	0.1937	5.34
„ -dimethylanilino-T.B.	0.3152	0.1791	0.1707	6.27
„ -diethylanilino-T.B.	0 2462	0.1522	0.1518	5.79
„ -benzalanilino-T.B.	0.3134	0.2078	0 2089	5.16
„ -dibenzylanilino-T.B.	0.2952	0.2208	0.2201	3.82
Di-*p*-aminodiethylanilino-T.B.	0.2562	0 1207	0.1199	7.99

TABLE II

Compounds of titanium tetrabromide with aromatic secondary amines. *

Amines.	Compound formed.	Colour	M.P.	% Titanium. Found.	Calc.	% Bromine. Found.	Calc.	% Nitrogen. Found	Calc.
Methyl-aniline	Tetramethyl-anilino-T.B. $[Ti(PhNH.Me)_4]Br_4$	Light yellow	236°	5.86	6.03	39.86	40.20	6 92	7.04
Ethyl-aniline	Tetra-ethyl-anilino-T.B. $[Ti(PhNH.Et)_4]Br_4$	Dirty white	242°	5.62	5.63	37.24	37.56	6.37	6 57
Benzyl-aniline	Tetra-benzyl-anilino-T.B. $[Ti(PhNH.CH_2Ph)_4]Br_4$	Leafy green	167°	4.28	4.36	29.24	22.09	5.12	5.09
Diphenyl-amine	Tetra-diphenyl-amino-T.B. $[Ti(^{Ph}_{Ph}>NH)_4]Br_4$	Yellowish white	226°	4.46	4 63	30.52	30.89	5.28	5 41

* No compound was formed with carbazole.

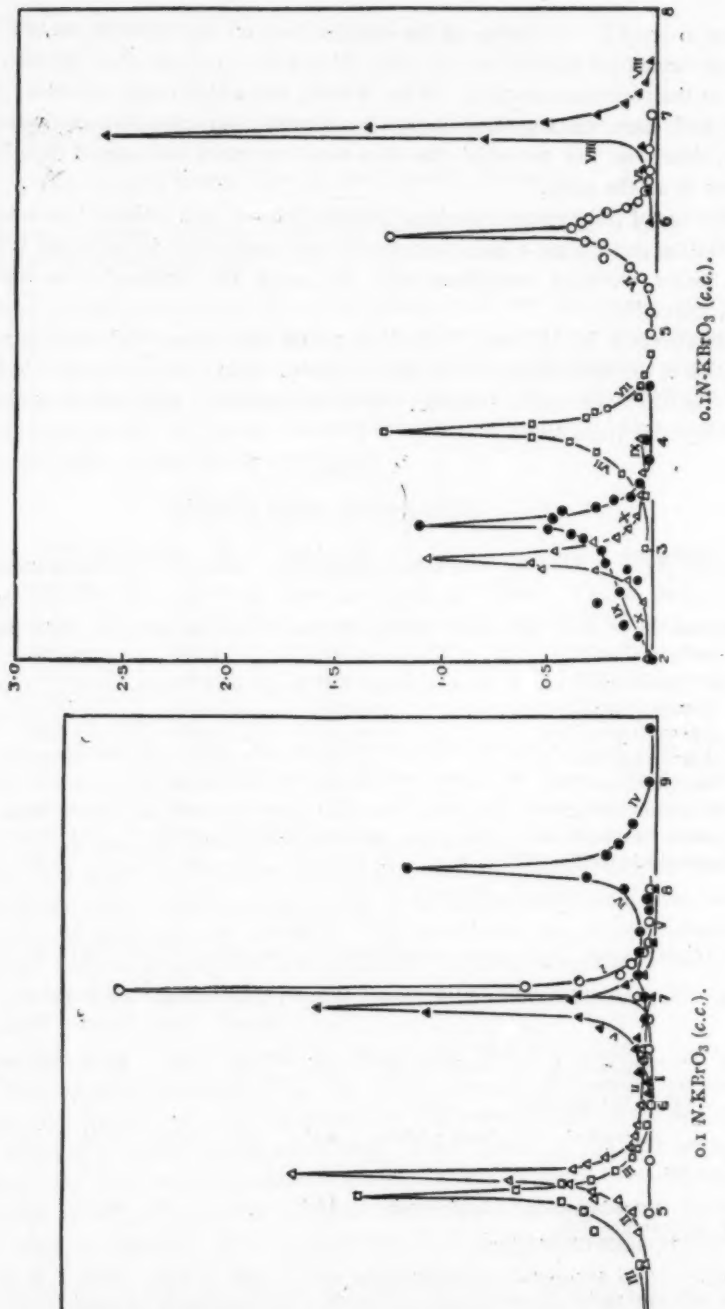

FIG. 1

FIG. 2

TABLE III

Compounds of titanium tetrabromide with aromatic tertiary amines.

Amines.	Compound formed.	Colour.	M.P.	% Titanium. Found.	% Titanium. Calc.	% Bromine. Found.	% Bromine. Calc.	% Nitrogen. Found.	% Nitrogen. Calc.
Dimethyl-aniline	Tetra-dimethyl-anilino-T.B. $[Ti(PhNMe_2)_4]Br_4$	Light grey	138° (decomp.)	5.58	5.63	37.24	37.56	6.38	6.57
Diethyl-aniline	Tetra-diethyl-anilino-T.B. $[Ti(Ph.NEt_2)_4]Br_4$	White	248°	5.02	4.58	33.02	33.20	5.64	5.81
Quinoline	Titra-quinolino-T.B. $[Ti(C_6H_4<^{CH:CH}_{N:CH})_4]Br_4$	Brownish grey	122°	4.41	5.43	35.82	36.20	6.21	6.33
Benzal-aniline	Tetra-benzal-anilino-T.B. $[Ti(PhCH:N\,Ph)_4]Br_4$	Deep yellow	160°	4.38	4.40	29.16	29.30	5.04	5.13
Dibenzyl-aniline	Tetra-dibenzyl-anilino-T.B. $[Ti\{Ph.N(CH_2.Ph)_2\}_4]Br_4$	Ash grey	154°	3.24	3.29	21.81	21.92	3.86	3.84
p Amino-di-ethyl-aniline	Di-*p*-amino-di-ethylanilino-T.B. $[Ti(Et_2N.C_6H_4.NH_2)_2]Br_4$	Black	305°	6.86	6.90	45.84	45.98	8.14	8.05

DISCUSSION

The compounds formed with titanium tetrabromide and the secondary and tertiary amines are in many respects similar to those formed with the primary amines. They are generally insoluble in organic solvents, but the compounds formed with diphenylamine, benzalaniline, dibenzylaniline, quinoline and *p*-aminodiethylaniline are soluble in chloroform, absolute alcohol and acetone, and insoluble in carbon tetrachloride, benzene and petroleum ether. Contact with water, sodium hydroxide or sodium carbonate sets in their hydrolysis, but complete hydrolysis takes place only when warmed at about 50° and titaninm hydroxide is precipitated according to the equations:

$$Ti(4\ Am.)Br_4 + 4H_2O \longrightarrow Ti(OH)_4 + 4\ Am.\ HBr$$

$$Ti(4\ Am.)Br_4 + 4NaOH \longrightarrow Ti(OH)_4 + 4NaBr + 4Am.$$

On heating alone they afford a sublimate, which is soluble in water, acidic and responds to the test for Br, : NH in secondary amines and N : in tertiary amines. The presence of secondary and tertiary amines was also confirmed in the aqueous extract by the standard methods. When they are heated with sodalime, the corresponding amines separate out and condense in the cooler parts of the tube, analogous to the behaviour of the compounds with primary amines (*loc. cit.*). The compounds formed

with dimethylaniline and quinoline and titanic bromide are very hygroscopic and begin to decompose on exposure. However, they are fairly stable at room temperature when kept in vacuum or in the perfectly dry air.

Di-*p*-aminodiethylanilino-titanic bromide is hygroscopic, but like the compounds formed with the primary diamines (*loc. cit.*) is very stable, and melts at a high temperature. It hydrolyses only after prolonged boiling with water or alkalies, which seems to be due to the formation of the chelate compound.

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SPECTROPHOTOMETRIC STUDY OF THE FERRIC THIOSULPHATE COMPLEX. PART III

By G. Mahapatra, C. Nanda and D. Patnaik

The extinction coefficient of the labile ferric thiosulphate complex at wave-length 500 mμ and the instability constant of the complex at ionic strength 0.12 have been determined. For the evaluation of the concentration of free $S_2O_3^{2-}$ ion, it is necessary to take into consideration the various side equilibria. With more such equilibria, the uncertainty increases in the calculation of free $S_2O_3^{2-}$ ion concentration. No foreign electrolyte has been used in our experiment, hence no new side equilibria except those inherent in the system are introduced. This has led to a more precise evaluation of the free $S_2O_3^{2-}$ ion concentration. The values for the extinction coefficient (500) and for the instability constant (1.057×10^{-2}) at 0.12 ionic strength of the complex are therefore reasonably accurate.

The coloured intermediate, $FeS_2O_3^+$, produced by the reaction of thiosulphate with ferric salts, is labile and its decay curve is S-shaped (Patnaik and Mahapatra, *Curr. Sci.*, 1955, **24**, 195). It has been observed by Schmidt (*Z. physikal. Chem.*, 1930, **148**, 321) that both the forward and back reactions

$$Fe^{3+} + S_2O_3^{2-} \rightleftharpoons FeS_2O_3^+ \quad \ldots \quad \ldots \quad (1)$$

are extremely rapid. Let $K_{FeS_2O_3^+}$ be the instability constant of the complex. Then

$$K_{FeS_2O_3^+} = \frac{[Fe^{3+}]\,[S_2O_3^{2-}]}{[FeS_2O_3^+]} \quad \ldots \quad \ldots \quad (2)$$

If the initial concentrations of Fe^{3+} and $S_2O_3^{2-}$ ions be a and b respectively and c, that of the intermediate $FeS_2O_3^+$ at zero time, *i.e.*, just at the moment of mixing the solutions of thiosulphate and the ferric salt, equation (2) reduces to

$$K_{FeS_2O_3^+} = \frac{(a-c)\,(b-c)}{c} \quad \ldots \quad \ldots \quad (3)$$

and since c is small, neglecting higher powers of c, we get

$$ab - c\,(a + b) = K_{FeS_2O_3^+}.\ c \quad \ldots \quad \ldots \quad (4)$$

According to Beer's law, the optical density D_{t_0} at zero time, *i.e.*, when the solutions are just mixed, becomes

$$D_{t_0} = \log \frac{I_0}{I \text{ at zero time}} = \epsilon.c.d$$

or

$$c = \frac{D_{t_0}}{\epsilon.d} \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where I_0 = intensity of the incident light; I at zero time = intensity of the transmitted light at zero time; d = the thickness of the liquid layer; ϵ = the extinction coefficient.

The value of I at zero time can be obtained as described previously (this *Journal*, 1956, **33**, 243). Substituting the value of c from equation (5) in equation (4) we get

$$ab - \frac{D_{t_0}}{\epsilon.d}(a + b) = K_{FeS_2O_3^+}.\frac{D_{t_0}}{\epsilon.d}$$

or

$$\frac{ab}{D_{t_0}} = \frac{a + b}{\epsilon.d} + \frac{K_{FeS_2O_3^+}}{\epsilon.d} \quad \ldots \quad \ldots \quad (6)$$

On the right side of equation (6), the term $K_{FeS_2O_3^+}$. $\epsilon.d$ is constant. In the term $(a + b)/(\epsilon.d)$ the numerator varies with change of a and b, while $1/\epsilon.d$ remains constant. It is evident that a straight line would be obtained by the plot of ab/D_{t_0} against $(a + b)$, the slope of which is equal to $1/\epsilon.d$. Since d is known, ϵ can be calculated which, on substitution in equation (5), gives the value of c. With the help of equation (3), $K_{FeS_2O_3^+}$ can also be evaluated.

EXPERIMENTAL

Solutions of sodium thiosulphate in water and that of ferric perchlorate in perchloric acid were used. So the ions inherent in the system are Fe^{3+}, Na^+, H^+, ClO_4^- and $S_2O_3^{2-}$. All side equilibria must involve these ions. The hydrogen-ion concentration was maintained at 0.05*N*. The concentrations of the thiosulphate and ferric perchlorate solutions were so chosen that the ionic strength was about 0.12. No new ions were introduced.

TABLE I

Log I of different composition ($R_1 \ldots R_7$) *against time.*

Time.	R_1 A−10 B−7.5	R_2 A−10 B−5.0	R_3 A−7.5 B−10	R_4 A−7.5 B−7.5	R_5 A−7.5 B−5.0	R_6 A−5.0 B−10	R_7 A−5.0 B−7.5
5 sec.	0.699	1.079	0.699	0 916	1.230	1.000	1.176
10	0.778	1.114	0.778	0 977	1.261	1.070	1.211
15	0.903	1 176	0.903	1.061	1.301	1.154	1.273
20	1 041	1.255	1 041	1.161	1.363	1.249	1 342
25	1.204	1.357	1.150	1.284	1.427	1.347	1.419
30	1.352	1 454	1.322	1.394	1.495	1.447	1.505
35	1.505	1.562	1 447	1.505	1.568	1.535	1.574
40	1.613	1.648	1 544	1.594	1.636	1.607	1.638
45	1.703	1.728	1 636	1.672	1.699	1.672	1.697
50	1.778	1 796	1.695	1.763	1.754	1.720	1.740
55	1.831	1.851	1 746	1.780	1.799	1.761	1.778
60	1.872	1.893	1.784	1.818	1.836	1.792	1.808
65	1.902	1.924	1.813	1.848	1.866	1.823	1.834
70	1.927	1.948	1.838	1.879	1.892	1.840	1.853
75	1.943	1.964	1.857	1.892	1.914	1.850	1.869
80	1.957	1.973	1.875	1.907	1.929	1.869	1.884
85	1.966	1.982	1.889	1.919	1.945	1.885	1.896
90	1.974	1.986	1.950	1 929	1.946	1.895	1.906
95	1 979	1.987	1 909	1.939	1.964	1.904	1.914
100	1.981	...	1.915	1.945	...	1.911	1.926

A and B are given in m. moles per litre where A = Fe^{3+} & B = $S_2O_3^{2-}$.

The experimental details for determining the concentrations of free Fe^{3+} and $S_2O_3^{2-}$ ions have been described previously (this *Journal*, 1956, **33**, 459).

In Table I, the logarithms of the transmitted light for different composition R_1, R_2, R_3,...of the reactants have been noted against time. A and B denote the actual concentrations (not the effective concentration) of ferric perchlorate and sodium thiosulphate in m. moles per litre. Wave-length used was 500 mμ and the working temperature was 25° ± 0.1°.

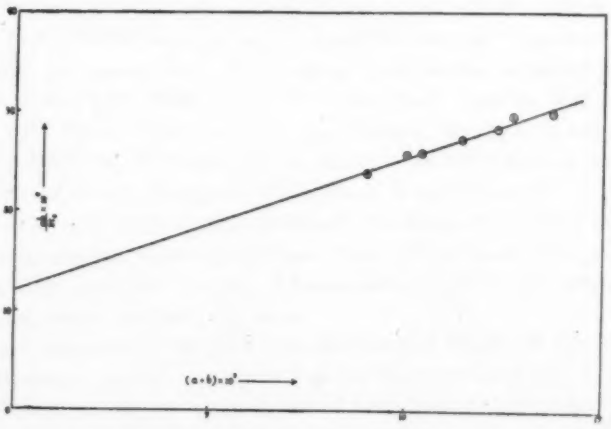
TABLE II

[Calculated values of *a*, *b* and *c* are expressed in m.moles per litre].

Compositions.	R_1.	R_2.	R_3.	R_4.	R_5.	R_6.	R_7.
$[Fe^{3+}] \times 10^3$ (*a*)	9.5	9.5	7.1	7.2	7.3	4.8	4.8
$[S_2O_3^{2-}] \times 10^3$ (*b*)	4.2	2.8	5.6	4.2	2.8	5.6	4.2
Log *I* at zero time	0.670	1.051	0.670	0.895	1.220	0.966	1.157
D_{t_0}	1.330	0.939	1.330	1.105	0.780	1.034	0.843
$\frac{ab}{D_{t_0}} \times 10^6$	30.00	28.36	29.90	27.36	25.76	25.99	23.91
$(a+b) \times 10^3$	13.70	12.30	12.70	11.40	10.00	10.40	9.00
$c \times 10^3$	1.77	1.25	1.77	1.47	1.04	1.38	1.12
$K_{Fe_2O_3^+} \times 10^2$	1.061	1.023	1.153	1.064	1.042	1.046	1.012

Table II shows the calculated values of the concentrations of Fe^{3+} and $S_2O_3^{2-}$ ions in m. moles per litre after taking into consideration all side equilibria as described

FIG. 1



previously (*loc. cit.*). The values of *I* at zero time obtained by extrapolation have also been recorded. The value of log I_0 for each case was 2 as 100% transmission

with the standard cell was always maintained. A straight line is obtained by the plot of ab/D_{t_0} against $(a+b)$. The slope of this line (Fig. 1) gives a value 1.333×10^{-3} for $1/\epsilon.d$. The thickness of the liquid layer was 1.5 cm, so the value of ϵ is 500. Since D_{t_0} for each of the compositions R_1, R_2, etc. are known, using the value of 500 for the extinction coefficient (ϵ), the value of c for each composition at zero time have been calculated from equation (5) and recorded in Table II. With the help of equation (3), the value of the instability constant has been calculated in each case. The average value of the constant of the complex for ionic strength 0.12 may be taken as 1.057×10^{-2} at 25°.

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SPECTROPHOTOMETRIC STUDY OF COPPER ALIZARIN SULPHONATE COMPLEX

By Anil K. Mukherji* and Arun K. Dey

Alizarin Red S forms coloured complexes with various metals and has been employed for the colorimetric determination of aluminium, uranium and thorium. The colour reactions, however, are not specific and are subject to interference by various metallic ions.

The formation of copper alizarin sulphonate has been investigated by the spectrophotometric method and Beer's law has been observed not to obey with different mixtures having varying amounts of copper and a large excess of the dye. The dye can be recommended as a colorimetric reagent for the determination of copper.

By Job's method of continuous variation the complex appears to possess the composition having the reactants in the ratio of 1:1. The value of the formation constant at 28° has been calculated to be $3.5 \pm 0.4 \times 10^5$ and free energy of formation to be -7.63 Kcals.

The structure of copper alizarin sulphonate has been discussed and it has been suggested that the two phenolic hydrogens are replaced by bipositive copper to form the complex

Sodium alizarin sulphonate (Alizarin Red S) is known to produce characteristic colour reactions with may inorganic ions. This property has been utilised in the colorimetric determination of metal ions in dilute solutions (Sandell, "Colorimetric Determination of Traces of Metals", Interscience, New York, 1950, p. 123). Alizarin Red S has also been successfully employed for the colorimetric determination of aluminium (Poole, "B.D.H. Book of Organic Reagents", 1949, p. 4) and the interference of various ions has been discussed by Parker and Goddard (*Anal. Chim. Acta*, 1950, **4**, 517). Raghava Rao and co-workers investigated the complex formation between Alizarin Red S and uranium and thorium (*ibid.*, 1955, **13**, 79, 142) and suggested the dye as a suitable reagent for the estimation of these metals. Ware (U.S. Atomic Energy Comm. Rep., MDDC, 1945, p. 1432), however, does not recommend the dye for the determination of uranyl ion. In a recent publication Mukherji and Dey (*Proc. Nat. Acad. Sci., India*, 1957, **26A**,) have shown that Alizarin Red S produces an orange colour with dilute solutions of copper sulphate, having a maximum absorption at 500 mμ ; they discussed the effect of p_H changes on the colour of the dye and have sought to explain the colour changes on the basis of Kuhn's formula (*J. Chem. Phys.*, 1948, **16**, 840; 1949, **17**, 1198) while considering the different ionising structures in the presence of varying concentrations of hydrogen ions. They have also investigated the composition, stability and free energy of formation of lead alizarin sulphonate complex by the spectrophotometric method (*loc. cit.*).

In the present communication the spectrophotometric study of the system $CuSO_4$-Alizarin Red S, using various concentrations of the reactants, has been made. The composition and structure of the complex formed have been discussed and the formation constant and the free energy of formation of the complex calculated at 28°.

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Experimental

Standard solutions of $CuSO_4$ (B.D.H. Anala R) and Alizarin Red S (B.D.H. Indicator) were prepared using double distilled water. For the measurement of optical density Unicam SP 500 spectrophotometer was employed and the measurements conducted in an air-conditioned room at 28°. The mixtures were kept at least for 15 minutes after mixing to attain equilibrium. For every measurement 1 cm thickness of the solutions was used in glass cells supplied along with the instrument.

Validity of Beer's Law.—In a set of experiments to a fixed quantity of the dye were added varying quantities of $CuSO_4$ solution, keeping in view that the amount of the dye always remained in large excess as compared to that of $CuSO_4$. The total volume was made constant by the addition of water and the optical densities of the different mixtures measured at a wave-length of 500 mμ. The observations were repeated at different concentrations of the dye and $CuSO_4$ and it was concluded that Beer's law was not rigidly obeyed.

Nature of Complexes formed.—In another set of experiments, mixtures containing varying proportions of copper : Alizarin Red S (*i.e.* 1 : 1, 1 : 2, 1 : 3 etc.) were prepared and the optical densities of the solutions at different wave-lengths in each case measured. In all the cases the maximum absorption occurred at a spectral region of 500 mμ, thus indicating the formation of only one complex with the reagent (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437).

Composition of the Complex.—Job's method of continuous variation (*Compt. rend.*, 1928, **180**, 928 ; *Ann. chim.*, 1928, *x*, **9**, 113) was adopted. The total volume in each case was kept 50 c.c. Some of the typical results are recorded in Tables I and II. It may be mentioned that at the dilution and wave-length used (500 mμ) copper sulphate solution had no absorption.

Table I

Volume of $CuSO_4$.	Volume of Dye.	$CuSO_4$ (c) $= 5M \times 10^{-4}$. Dye (c') $= 5M \times 10^{-4}$. p_H of the mixtures = 3.7 to 4.1. $p = c'/c = 1$. Optical density of the Mixture.	Dye.	$CuSO_4$ (c) $= 3.33M \times 10^{-4}$. Dye (c') $= 3.33M \times 10^{-4}$. p_H of the mixtures = 3.9 to 4.3 $p = c'/c = 1$. Optical density of the Mixture	Dye.	$CuSO_4$ (c) $= 2.5 \times 10^{-4}$. Dye (c') $= 2.5 \times 10^{-4}$. p_H of the mixtures = 4.0 to 4.4. $p = c'/c = 1$. Optical density of the Mixture.	Dye.
0 c.c.	50 c.c.	0.190	0.190	0.150	0.150	0.110	0.110
5	45	0.310	0.180	0.230	0.140	0.180	0.100
10	40	0.400	0.160	0.300	0.130	0.250	0.100
15	35	0.470	0.140	0.330	0.100	0.280	0.090
20	30	0.500	0.125	0.370	0.080	0.310	0.080
25	25	0.520	0.110	0.380	0.070	0.320	0.070
30	20	0.490	0.100	0.370	0.070	0.300	0.060
35	15	0.450	0.070	0.330	0.050	0.260	0.050
40	10	0.360	0.060	0.260	0.035	0.210	0.040
45	5	0.220	0.050	0.140	0.020	0.120	0.030

The peaks of the curves occur at a ratio of 1 :1.

TABLE II

	Conc. of $CuSO_4$ (c) = $5.0M \times 10^{-4}$. Conc. of the dye (c') = $3.33M \times 10^{-4}$. p_H of the mixtures = 3.7 to 4.2. $p = c'/c' = 2/3$.			Conc. of $CuSO_4$ (c) = $3.33M \times 10^{-4}$. Conc. of the dye (c') = $5.00M \times 10^{-4}$. p_H of the mixtures = 3.9 to 4.2. $p = c'/c = 3/2$.		
Volume of $CuSO_4$.	Dye.	Optical density of the Mixture. (a)	Dye. (b)	Diff. (a-b)	Optical density of the Mixture (a)	Dye (b)	Diff. (a-b)
0 c.c.	50 c.c.	0.150	0.150	...	0.190	0.190	...
5	45	0.310	0.140	0.170	0.290	0.180	0.110
10	40	0.370	0.130	0.240	0.350	0.160	0.190
15	35	0.410	0.100	0.310	0.400	0.140	0.260
20	30	0.440	0.080	0.360	0.430	0.125	0.305
25	25	0.430	0.070	0.360	0.450	0.110	0.340
30	20	0.420	0.070	0.350	0.440	0.100	0.340
35	15	0.380	0.050	0.330	0.410	0.070	0.340
40	10	0.290	0.035	0.255	0.340	0.060	0.280
45	5	0.140	0.020	0.120	0.210	0.050	0.160

The peaks of the curves occur at a ratio of 1 : 1.

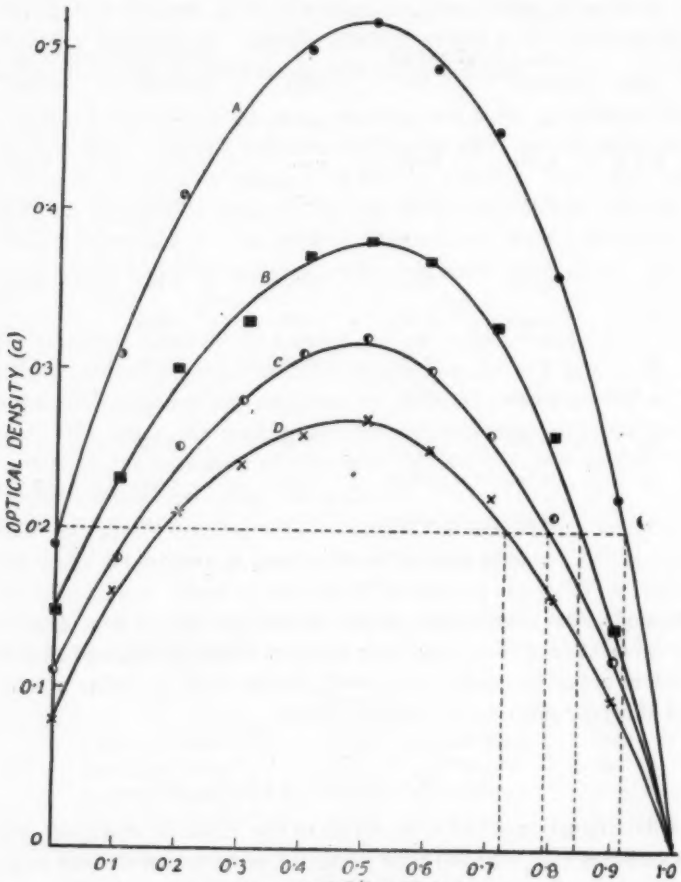
We conclude that only one complex forms at a ratio of 1 : 1 of the reactants. It may further be mentioned that it has been experimentally ascertained that no appreciable change in colour occurs in the dye for a small change in the p_H value which accompaines the addition of copper sulphate to Alizarin Red S.

DISCUSSION

For the determination of the composition of the coloured complex, Job's method of continuous variation (*loc. cit.*) has been employed using optical density as a guide of the complex formation. For a constant total concentration of the metallic ion and complexing agent, the concentration of the complex is greatest when metal and complexing agent are present in the system in the ratio in which they exist in the complex (cf. Martell and Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, New York, 1953, p. 29). If the complex is the only coloured substance present in the system, the optical density of the solution is proportional to the concentration of the complex. Hence, a graph, showing the variation of optical density with composition of the system, would afford a curve with a maximum at the composition corresponding to the formula of the complex. In our case, however, the dye has an absorption in the same region as the complex, whereas cupric ions do not show any absorption at the wave-length and dilution employed. Job (*loc. cit.*) stated that the method was not applicable to systems

in which more than one compound was formed, while Vosburgh and Cooper (*loc. cit.*) were able to apply the method to a special case in which they determined the equilibria involving three chelate compounds.

FIG. 1



For the determination of the stability constants we have employed the data plotted in Fig. 1, where the observed optical density (not the difference in optical density) has been plotted against $[Cu^{2+}]/([Cu^{2+}]+[R])$. It may be assumed that in the descending portion of the curve, where Cu^{2+} ions are in excess, most of the dye is bound up in the complex and therefore the optical density of the free dye does not contribute substantially to the optical density of the system. Hence, the observed optical density is mainly due to the colour of the complex. We may therefore assume that in curves A, B and C at the points, where the optical densities are the same (say 0.2), the amounts of complex formed are identical.

For the system : $mA + nB = A_mB_n$

where $(m/n = 1$, or $m = n = 1)$ the formation constant

$$K = \frac{x}{(a-x)\ (b-x)} \qquad \ldots \qquad \ldots \quad (1)$$

where x is the concentration of the complex, and a and b are the initial concentrations of $CuSO_4$ and Alizarin Red S respectively. Taking the two concentrations a_1 and a_2 and b_1 and b_2 of the reactants, giving the same optical density, that is, the same values of x_1 and x_2, we have

$$K = \frac{x}{(a_1-x)\ (b_1-x)} = \frac{x}{(a_2-x)\ (b_2-x)} \qquad \ldots \quad (2)$$

or

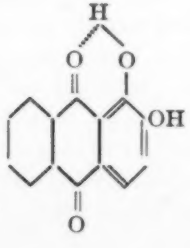
$$x = \frac{a_1b_1 - a_2b_2}{(a_1-b_1)-(a_2-b_2)} \qquad \ldots \quad (3)$$

Knowing the value of x in equation (3), the value of K can be found out by substitution in equation (1).

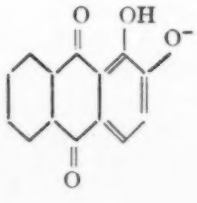
We have calculated the values of the formation constant (at 0.2 of the optical density in the curves A, B and C of Fig. 1) and the average value comes out to be $3.5 \pm 0.4 \times 10^5$. The dissociation constant therefore works out to be 2.86×10^{-6}. The free energy in terms of the dissociation constant K_d is represented by $\Delta F = RT \log K_d$, where the terms have their usual significance. In this system the value of ΔF at a temperature of 28° works out to be -7630 calories.

It is customary to calculate the values of the formation constant by "swamping" the complexing agent with simple ions in order to obtain systems of constant ionic strength. It was not possible in our case, because the dye itself was susceptible to colour changes by the addition of neutral salts like KCl, NaCl etc. Moreover, the solutions employed by us were extremely dilute and were of the order of 10^{-4} M.

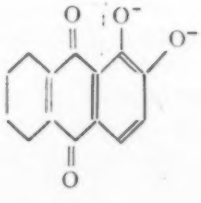
Alizarin Red S is capable of existing in three ionisable forms depending upon the p_H of the medium. The alizarin molecule can be represented by the following three structures :



(I)

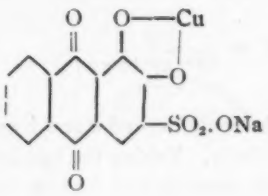


(II)



(III)

Since the ratio of the reactants for the formation of the complex is 1 : 1, the value of $[Cu^{2+}]/([Cu^{2+}]+[R])$ being 0.5 at the peaks of the curves, the structure of the complex is likely to be



similar to zirconyl and hafnyl alizarinates, as investigated by Leibhafsky and Winslow (*J. Amer. Chem. Soc.*, 1947, **69**, 1130) and Larsen and Hirozawa (*J. Inorg. Nuclear Chem.*, 1956, **3**, 198).

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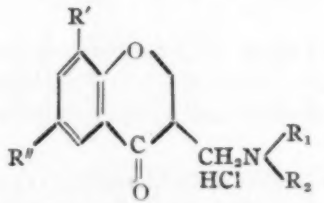
POSSIBLE ANTIAMOEBIC AGENTS. PART II. MANNICH BASES FROM CHLOROCHROMAN-4-ONES

By A. B. Sen and Yashwant D. Kulkarni

Mannich bases from 6-chloro-, 8-chloro- and 6:8-dichloro-chroman-4-ones have been prepared with a view to testing them for antiamoebic activity.

In view of the close resemblance of chromanones to the naturally occurring compounds such as flavones, flavanones, chromones and coumarins and the common occurrence of the basic side chains in the therapeutically active compounds, it was deemed worthwhile to incorporate basic groups into chromanones and to study their acitivity on lower organisms. Wiley (*J. Amer. Chem. Soc.*, 1951, **73**, 4205) has observed interesting amoebacidal acitivity in several Mannich bases (Ia), prepared from substituted chromanones. The presence of halogen atoms in important amoebacides, viz., vioform and diiodoquin, prompted the authors to synthesise Mannich bases (Ib) from monochloro- and dichloro-chromanones with a view to studying the effect of chlorine atoms on the amoebacidal acitivity.



[Ia : R′ & R″ = various groups]
[Ib : R′ & R″ = chlorine atoms]

In the present investigation chromanones were prepared from *o*-chloro-, *p*-chloro- and 2:4-dichloro-phenols by the action of β-propiolactone (cf. Gresham *et al.*, *ibid.*, 1949, **71**, 661), followed by cyclisation of the resulting β-(mono- or dichlorophenoxy)-propionic acids with either concentrated sulphuric acid (98%) (cf. Hurd and Hayao, *ibid.*, 1954, **76**, 5065) or with phosphorus pentoxide in benzene (cf. Chakravarti and Dutta, this *Journal*, 1939, **16**, 639).

Among the methods available for cyclisation of β-phenoxypropionic acids to chromanones, that of Hurd and Hayao, using concentrated sulphuric acid was found to be more convenient. From β-(2:4-dichlorophenoxy)-propionic acid, 89% yield of 6:8-dichlorochromanone was obtained. But in the cyclisation of β-(*o*-chlorophenoxy)- propionic acid to 8-chlorochromanone by the same method, only 28% of the cyclised product was obtained. By the method of Chakravarti and Dutta (*loc. cit.*), using phosphorus pentoxide in dry benzene, the yield was, however, improved to 76%.

The Mannich reaction in chromanones, as described by Harradence *et al.* (*J. Proc. Roy. Soc.*, N. S. Wales, 1939, **27**, 273) employing equimolar quantities of a chromanone, paraformaldehyde and secondary amine hydrochloride in absolute alcohol as a solvent, afforded very low yields (less than 5%) of the desired Mannich bases (Ib). But by substituting dry benzene as the solvent and acidifying the reaction mixture at the start of the reaction with a few drops of A. R. HCl and increasing the time of the reaction to 6 hours, we have obtained 80% yield of the Mannich product with 6 : 8-dichlorochromanone, paraformaldehyde and morpholine hydrochloride.

All the Mannich bases (as hydrochlorides) (Ib) were found to be stable, but the aqueous solutions on standing for a long time decomposed and deposited insoluble oils. The isolation of bases from (Ib) yielded sticky semi-solids which were not crystallisable. However, the bases were characterised through their picrates.

The total failure of the Mannich reaction was observed with diethylamine hydrochloride in the case of all the three chromanones used.

EXPERIMENTAL

o-Chloro-, *p*-chloro- and 2 : 4-dichloro-phenols were distilled before use. β-Propiolactone was supplied by Eastman Kodak Company. The three β-(mono- and dichlorophenoxy)-propionic acids were obtained from the above phenols by following the method of Gresham *et al.* (*loc. cit.*).

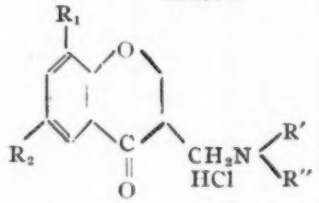
Chromanones.—The cyclisation of β-phenoxypropionic acids into chromanones was effected either by (*i*) H_2SO_4 (conc.) or (*ii*) by P_2O_5 in benzene. The method (*i*) used for the preparation of 6 : 8-dichloro- and 6-chloro-chromanones was essentially that of Hurd and Hayao (*loc. cit.*).

6 : 8-*Dichlorochromanone.*—β-(2 : 4-Dichlorophenoxy)- propionic acid (22 g.) was dissolved in 98% H_2SO_4 (220 c. c.). The yellow-brown solution was kept at room temperature (25°) for 36 to 48 hours, stirred occasionally, and poured over crushed ice (2 kg.), when 18 g. (89%) of the crude chromanone, m.p. 84-85°, was obtained. It was washed with sodium bicarbonate solution and then thoroughly with cold water. On drying and recrystallising from ethyl alcohol pure, white, crystalline chromanone was obtained, m.p. 86°-87°, yield 17 g. The 2 : 4-dinitrophenylhydrazone melted at 278-79° with decomposition. (Found : N, 14.0. Calc. N, 14.1%).

6-*Chlorochromanone* was prepared starting from β-(*p* chlorophenoxy) -propionic acid (21 g.) and following the same procedure, m.p. 101° (lit. m.p. 106°), yield 16 g. (84%).

8-*Chlorochromanone.*—The method (*ii*) used for preparing this chromanone was essentially that of Chakravarti and Dutta (*loc. cit.*). *o*-Chlorophenoxypropionic acid (5 g.) was dissolved in dry benzene (100 c.c.) and the solution was refluxed with P_2O_5 (15 g.) for 10 hours. The supernatant benzene layer was decanted off and the brown residue was decomposed by crushed ice and then extracted with benzene. The benzene extract was washed with sodium bicarbonate solution and then with water and finally dried over calcium chloride. The benzene was distilled off under reduced pressure and the brown residue (3.6 g., 76%) was crystallised from alcohol in light yellow needles, m.p. 65°.

TABLE I



Sl. No.	R_1 and R_2.	R′ and R″.	M.P.	Yield.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	Picrates M.P.	Picrates Formula.	Picrates % Nitrogen. Found.	Picrates % Nitrogen. Calc.
1.	6-Chloro-	Dimethyl	150°	36.3%	$C_{13}H_{15}O_2NCl_2$	5.21	5.07	53.00	52.20	5.50	5.44	136°	$C_{18}H_{17}O_9N_4Cl$	11.30	11.95
2.	,,	Piperidyl	214°	63.3	$C_{15}H_{19}O_2NCl_2$	4.22	4.43	...	...	...	...	158°	$C_{21}H_{21}O_9N_4Cl$	10.92	11.01
3.	,,	Morpholinyl	164°	65.1	$C_{14}H_{17}O_3NCl_2$	4.31	4.40	52.30	52.84	5.00	5.34	162°	$C_{20}H_{19}O_{10}N_4Cl$	11.34	11.00
4.	,,	Benzyl	198°	88.8	$C_{17}H_{17}O_2NCl_2$	4.23	4.14	59.80	60.35	5.10	5.03	...		...	...
5.	8-Chloro-	Dimethyl	164°	44.0	$C_{13}H_{15}O_2NCl_2$	4.98	5.07	51.60	52.20	5.40	5.44	142°	$C_{18}H_{17}O_9N_4Cl$	11.65	11.95
6.	,,	Piperidyl	202°	80.0	$C_{15}H_{19}O_2NCl_2$	4.18	4.43	56.34	59.97	6.20	6.01	155°	$C_{21}H_{21}O_9N_4Cl$	10.68	11.01
7.	,,	Morpholinyl	172°	40.0	$C_{14}H_{17}O_3NCl_2$	4.30	4.40	...	...	...	...	...			...
8.	,,	Benzyl	194°	78.8	$C_{17}H_{17}O_2NCl_2$	4.21	4.14	...	...	...	...	183°	$C_{23}H_{19}O_9N_4Cl$	10.01	10.56
9.	6:8-Dichloro-	Dimethyl	168°	35.3	$C_{13}H_{14}O_2NCl_3$	4.62	4.51	...	...	...	...	165°	$C_{18}H_{16}O_9N_4Cl_2$	10.24	10.90
10.	,,	Piperidyl	208°	35.5	$C_{15}H_{18}O_2NCl_3$	3.89	3.99	50.58	51.36	5.00	5.13	148°	$C_{21}H_{20}O_9N_4Cl_2$	10.01	10.32
11.	,,	Morpholinyl	178°	80.0	$C_{14}H_{16}O_3NCl_3$	4.09	3.98	47.00	47.68	4.10	4.54	155°	$C_{20}H_{15}O_{10}N_4Cl_2$	10.42	10.31
12.	,,	Benzyl	202°	47.0	$C_{17}H_{16}O_2NCl_3$	3.45	3.76	...	...	...	...	...		...	...

3-Dialkylaminomethylchroman-4-one Hydrochlorides (Ib) : *Mannich Reaction.*— A mixture of a chromanone (0.01 *M*) and paraformaldehyde (0.01*M*) in 25 c.c. of dry benzene was heated under reflux for 30 minutes. To this was added (0.01*M*) of a secondary or primary amine hydrochloride. (The amines used were dimethylamine, piperidine, morpholine and benzylamine hydrochlorides). The reaction mixture was acidified with a few drops of HCl and refluxed for 6 hours, during which most of the Mannich bases (Ib) separated in pure crystalline form. After cooling, the reaction mixture was filtered and the product obtained was washed repeatedly with dry benzene and finally recrystallised from absolute alcohol. The Mannich bases (Ib) were characterised by preparing their picrates.

Picrates.—The compound (Ib : 0.5 g.) was dissolved in hot water (10 c.c.) and mixed with a saturated aqueous solution of picric acid (10 c.c.). An immediate turbidity appeared and crystalline picrate separated on cooling. This was filtered, washed thoroughly with water and finally recrystallised from ethyl alcohol.

Decomposition of the Mannich Bases (Ib).—The compounds (No. 1, 6 and 11 listed in Table I) (1g. each) were dissolved separately in 10 c. c. of water. Deposition of insoluble oil was observed in each case after 36 hours' standing at room temperature.

The m. p., yield and the analysis of the Mannich bases (Ib) and their picrates are recorded in Table I.

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POTENTIOMETRIC STUDIES ON THE COMPOSITION OF NICKEL FERROCYANIDE COMPLEX

By Ram Sahai Saxena

The formation and precipitation of nickel ferrocyanide has been studied by potentiometric titrations between nickel sulphate and potassium ferrocyanide using ferri-ferrocyanide electrode both by the direct and the inverse methods. The point of inflection obtained from the maximum value of $\Delta E/\Delta C$ corresponds to the formation of a double salt having the composition $4Ni_2Fe(CN)_6 . 3K_4Fe(CN)_6$, with either of the substances used as the reagent. The potentiometric curves have a regular shape; a sharp break in potential occurs at the equivalence point and the titration results are accurate and reproducible. The effect of alcohol on the end-point as well as on the nature of curves has been studied.

The reaction between nickel salts and $K_4Fe(CN)_6$ has been investigated by several workers by purely analytical methods and also by physico-chemical methods, but there is hardly any co-ordination of the views expressed by them. Werner (*Z. anal. Chem.*, 1919, **58**, 23) reported the quantitative precipitation of a bluish green compound $Ni_2Fe(CN)_6$. Treadwell and Chervet (*Helv. Chim. Acta.*, 1922, **5**, 633) suggested the composition as $K_2NiFe(CN)_6$. Gasper *et al.* (*Anal. Fis. Quim.*, 1926, **24**, 323) reported that the nickel ferrocyanide was possibly a double, complex or associated salt. Rene Paris (*Compt. rend.*, 1934, **199**, 863) showed that the composition of nickel ferrocyanide was between $K_2NiFe(CN)_6$ and $Ni_4K_4[Fe(CN)_6]_3$. Velculescu (*Bull. Chim. Soc. Romania*, 1933, **34**, 471) reported that ferrocyanide of nickel was not a pure compound but probably a mixture of $3K_2NiFe(CN)_6$ and $Ni_2Fe(CN)_6$. Wyrubow (*Annalen*, **8**, 444) observed that the composition of the precipitate changed from $K_2NiFe(CN)_6$ to $K_2Ni_3[Fe(CN)_6]_2$ on addition of excess of ferrocyanide. Tananaev and Levina (*Zhur. Anal. Khim.*, 1946, **1**, 224) studied the reaction between $NiSO_4$ and $K_4Fe(CN)_6$ electrolytically, colorimetrically and turbidimetrically and showed that the reaction proceeded in three stages: $Ni_2Fe(CN)_6$, $Ni_2Fe(CN)_6 . 2K_4Fe(CN)_6$, and in the third phase, a double salt $2Ni_2Fe(CN)_6 . K_4Fe(CN)_6$ was formed. With $Na_4Fe(CN)_6$ the precipitate had the composition $Na_2Ni_3[Fe(CN)_6]_2$ and with $Li_4Fe(CN)_6$, $Ni_2Fe(CN)_6$ was quantitatively precipitated.

In view of the conflicting opinions and in the absence of any decisive views on the composition of nickel ferrocyanide, it was considered worthwhile to make its detailed study by physico-chemical methods to obtain more conclusive evidences on the composition of complex metallic ferro- and ferricyanides (Saxena *et al.*, *Z. anorg. Chem.*, 1956, **285**, 90; 1954, **276**, 204; this *Journal*, 1951, **28**, 141, 222, 703; 1952, **29**, 263, 284, 529, 535; 1954, **31**, 53, 56, 157 etc.). In this paper only the results of potentiometric titrations have been included and discussed.

Experimental

Merck's guaranteed extrapure reagents [$NiSO_4$ and $K_4Fe(CN)_6$] were used. The strenghths of the solutions were estimated by standard methods of analysis. Using

different concentrations of the two salts in solution, the titrations were performed both by the direct and the inverse methods [*i.e.*, when $K_4Fe(CN)_6$ was added from the microburette to $NiSO_4$ in the titration cell and *vice-versa*]. Potassium ferrocyanide solution containing 1% potassium ferricyanide was used to make ferri-ferrocyanide electrode (Kolthoff and Furman, 'Potentiometric Titrations", New York, 1947, p. 323). A platinised platinum foil was used as an indicator electrode in conjunction with a saturated calomel electrode. The E.M.F. was measured on a Cambridge p_H-meter. The titrations were also carried out in presence of alcohol up to a total concentration of 20% by volume. Curves were plotted between the volume of the titre and the E observed and from the sharp jump in potential, indicated by the titration curves, the end-point could be found out ; this was further checked by calculating the maximum value of $\Delta E/\Delta C$ in each case. The reagent (20 c.c.) was taken in the electrode vessel each time. For the sake of brevity only two figures have been given, one for the direct and the other for reverse titrations.

TABLE I

Summary of results of potentiometric titrations.

$K_4Fe(CN_6$.	$NiSO_4$.	Calc.	Points of equivalence required for the formation of $4Ni_2Fe(CN)_6.3K_4Fe(CN)_6$ observed from $\Delta E/\Delta C$ in presence of 0% alcohol.	10% alcohol.	20% alcohol.
		Direct titrations.			
$M/5$	$M/20$(20 c.c.)	4.375 c.c.	4.20 c.c.	4.30 c.c.	4.35 c.c.
$M/20$	$M/100$ (,,)	3.50	3.40	3.45	3.50
		Reverse titrations.			
$M/20$(20 c.c.)	$M/5$	5.70 c.c.	5.80	5.75	5.70
$M/100$ (,,)	$M/20$	4.57	4.70	4.60	4.55

DISCUSSION

From the strength of solutions of $K_4Fe(CN)_6$($M/5$ and $NiSO_4M/20$) the calculated titre values for the formation of the more probable compounds are given below.

1. Titre values for 20 c c. of $M/20$-$NiSO_4$ in direct titrations ...	$K_2NiFe(CN)_6$. 5 0 c c.	$Ni_2Fe(CN)_6$. 2.5 c.c.	$4Ni_2Fe(CN)_6.3K_4Fe(CN)_6$. 4.375 c.c	
	[$M/5$-$K_4Fe(CN)_6$ solution]			
2. Titre values for 20 c.c. of $M/20$-$K_4Fe(CN)_6$ in reverse titrations ...	5.0 c.c.	10.0 c.c.	5.71 c.c.	
	[$M/5$-$NiSO_4$ solution]			

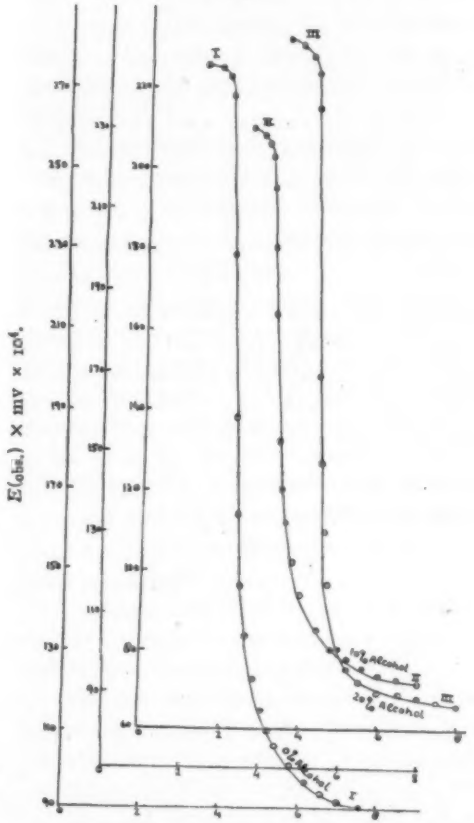
The titre values required for the formation of the above compounds, employing different concentrations of reactants, can be calculated accordingly both in the direct and the reverse titrations.

It is clear from Figs. 1-2 and Table I that the reaction between $NiSO_4$ and $K_4Fe(CN)_6$ can be successfully followed potentiometrically, applying ferri-ferrocyanide electrode with either of the substances used as the reagent. The point of inflection calculated from the maximum values of $\Delta E/\Delta C$ occurs at a stage where the molecular ratio of reactants,

$K_4Fe(CN)_6 : NiSO_4$ is as 7:8 and corresponds to the formation of the compound $4Ni_2Fe(CN)_6.3K_2Fe(CN)_6$, and is much different from those required for the formation of other probable compounds, $K_2NiFe(CN)_6$ and $Ni_2Fe(CN)_6$, as reported earlier (*loc. cit.*).

FIG 1

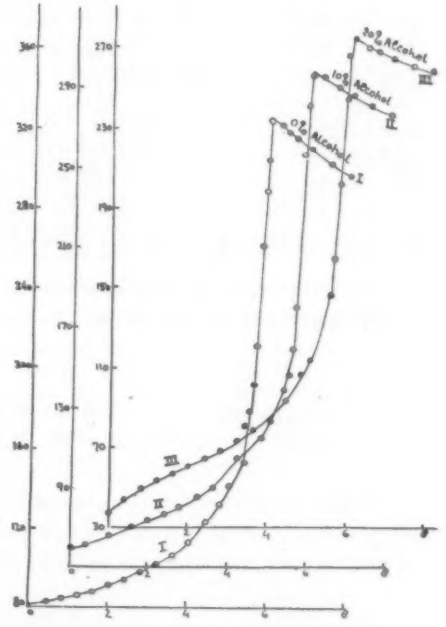
Direct titration.



$M/4$-$K_4Fe(CN)_6$ added to 20 c.c. $M/2$-$NiSO_4$ (*c.c.*).

FIG. 2

Reverse titration.



$M/5$-$NiSO_4$ added to 20 c.c. $M/2$ $K_4Fe(CN)_6$ (*c.c.*).

The titration curves have a regular shape, there is a sharp jump in potential at the end-point and the results are accurate and reproducible. In direct titrations, the potential does not remain steady in the beginning of the reaction, but assumes a steady value before the end-point; in the inverse titrations, however, the E.M.F. gradually rises from the beginning, potential becomes constant after each addition of the break and a sharp jump is observed at the end-point. In alcoholic solutions the break in potential is less than that in aqueous solution although the nature of titration curves remains unchanged in both cases.

It is evident from Table I that the observed titre values in direct titrations are slightly lower than the calculated points of equivalence in aquous medium; while in

the case of reverse titrations, they are slightly higher. In the presence of increasing amounts of alcohol, the observed titre values in both cases gradually approach the calculated values more closely.

The discrepancy between the observed and the calculated titre values in aqueous medium and the subsequent change when the titrations are carried out in alcoholic medium, supports our views on the adsorptive and hydrolytic behaviour of such ferro- and ferricyanide complexes (cf. Saxena *et al.*, *loc. cit.*).

In direct titrations, adsorption of Ni^{2+} ions by the precipitate would tend to lower the titre values in aqueous medium. In the reverse titrations, nickel ferrocyanide on hydrolysis would release some $Fe(CN)_6^{4-}$ ions which will consume some extra amount of $NiSO_4$, howsoever little it may be, and hence, the amount of nickel sulphate required will be slightly greater than the calculated equivalent. Alcohol suppresses adsorption and hydrolysis, and hence, a closer approach to the theoretical values is envisaged by the experimental results. In presence of 20% alcohol, the observed titre values almost coincide with the calculated ones.

The results of potentiometric titrations suggest that nickel ferrocyanide is not a pure compound but is a double salt represented by the formula $4Ni_2Fe(CN)_6.3K_4Fe(CN)_6$. The formation of the double salt was also suggested by Tananaev and Levina by electrochemical methods (*loc. cit.*) and by Gasper (*loc. cit.*). There is no evidence of the formation of $K_2NiFe(CN)_6$, as suggested by Treadwell and Chervet (*loc. cit.*).

Quantitative work on adsorption and hydrolysis in the case of nickel ferrocyanide is in progress and the results will be communicated shortly.

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STUDIES ON 3-*m*-TOLYL-2 : 4-THIAZOLIDIONE AND 5-ARYLAZO-3-PHENYL-2-PHENYLIMINO-4-THIAZOLIDONES

By P. N. Bhargava, A. J. Pantulu and R. P. Rao

3-*m*-Tolyl-2 : 4-thiazoildione has been condensed with aldehydes and its degradation products as well as characteristic reactions have been studied. Further 5-arylazo-3-phenyl-2-phenylimino-4-thiazolidones have been obtained by condensing 3-phenyl-2-phenylimino-4-thiazolidone with aryl diazonium chlorides.

In continuation to the earlier work on 3-aryl-2 : 4-thiazolidiones (Bhargava *et al.*, this *Journal*, 1955, **32**, 463 ; 1956, **33**, 596), it was considered worthwhile to prepare 3-*m*-tolyl-2 : 4-thiazolidione and 3-phenyl-2-phenylimino-4-thiazolidone.

The thiazolidione has been obtained by the interaction of *S*-di-*m*-tolylthiourea with monochloroacetic acid in glacial acetic acid and the thiazolidone prepared by the interaction of *S*-diphenylthiourea with monochloroacetic acid in absolute alcohol in the presence of anhydrous sodium acetate. The reactive methylene group of the thiazolidione has been successfully condensed with six aromatic aldehydes and that of the thiazolidone with six aryl diazonium chlorides, yielding respectively 5-arylidene-2 : 4-thiazolidiones and 5-arylazo-substituted thiazolidones. The attachment of the azo group to $-CH_2-$ group in position-5 in α-position to the activating carbonyl group is justified by the arguments advanced by Meerwein *et al.* (*J. prakt. Chem.*, 1939, **152**, 237) and is further supported by the observation that when the $-CH_2-$ group in position-5 of the thiazolidone nucleus is blocked by condensation with aromatic aldehydes, no azo dye is formed.

Further, mercuration of 3-*m*-tolyl-2 : 4-thiazolidione with mercuric acetate has yielded 3-acetoxymercuri-*m*-tolyl-2 : 4-thiazolidione. The acetoxymercuri group is assumed to enter the aryl nucleus.

The thiazolidione on decomposition with KOH has yielded *m*-toluidine, as confirmed by the preparation of its azo-β-naphthol derivative, and on oxidation with $KMnO_4$ in glacial acetic acid, 3-*m*-tolyl-2 : 4-thiazolidione-sulphone, as confirmed by analytical data.

Experimental

3-m-*Tolyl-2 : 4-thiazolidione* was prepared according to the method of Markley and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 2137) in glacial acetic acid in needles, m.p. 90°. (Found : S, 15.56. $C_{10}H_9O_2NS$ requires S, 15.49%).

3-m-*Tolyl-5-benzylidene-2 : 4-thiazolidione.*—A mixture of thiazolidione (0.5 g.) and benzaldehyde (0.35 g.), dissolved in glacial acetic acid (12 c.c.), and fused sodium acetate (1 g.) was heated under reflux for 1½ hours. On pouring the contents into water, a yellow precipitate was obtained. After keeping overnight, the yellow precipitate was filtered off and the product was crystallised from alcohol.

Similarly other aldehydes were condensed, yielding 5-arylidene derivatives. The properties and analytical data of these derivatives are recorded in Table I.

TABLE I

3-m-*Tolyl*-5-*arylidene*-2 : 4-*thiazolidione*.

Aldehyde.	% Yield.	M.P.	Sulphur%. Found.	Calc.
Benzaldehyde	65	105°	10.80	10.84
m-Nitrobenzaldehyde	60	201°	9.36	9.41
Vanillin	75	150°	9.32	9.30
Anisaldehyde	72	72°	9.80	9.84
Cinnamaldehyde	70	100°	9.89	9.06
Piperonal	68	116°	9.46	9.43

Decomposition of 3-m-*tolyl*-2 : 4-*thiazolidione*.—The thiazolidione (1 g.) was boiled with 40% KOH (50 c.c.) on a water-bath for 2 hours. The reaction mixture on distillation gave a liquid, which was confirmed as *m*-toluidine by the preparation of its azo-β-naphthol derivative, m.p. 140°.

3-*Acetoxymercuri*-m-*tolyl*-2 : 4-*thiazolidione*.—The thiazolidione (1 g.) was dissolved in glacial acetic acid (18 c.c.) and to this absolute alcohol (15 c.c.) and mercuric acetate (1.5 g.), dissolved in water (15 c.c.) and acidified with acetic acid, were added. After 24 hours, a precipitate was obtained, which was filtered, washed respectively with dilute acetic acid and hot water, and crystallised from alcohol in a pale yellow form, m.p. 265°. (Found : Hg, 42.78. $C_{12}H_{11}O_4NSHg$ requires Hg, 43.08%).

3-m-*Tolyl* - 2 : 4 - *thiazolidione* - *sulphone*.—3-*m*-Tolyl-2 : 4-thiazolidione (1 g.) was dissolved in glacial acetic acid (20 c.c.) and treated slowly with $KMnO_4$ (1 g.), dissolved in water (40 c.c.), at 0°. The precipitate, obtained after removing excess of $KMnO_4$ and chilling, was washed with ice-water, dried and crystallised from absolute alcohol in a yellow form, m.p. 116°. (Found : C, 50 14 ; H, 3.80 ; N, 5.90 ; S, 13.32. $C_{10}H_9O_4NS$ requires C, 50.20 ; H, 3.76 ; N, 5.85 ; S, 13.38%).

2-*Phenylimino*-3-*phenyl*-5-*phenylazo*-4-*thiazolidone* was prepared by the method of Bhargava and Goswami (this *Journal*, 1955, **32**, 763). Similarly the thiazolidone was condensed with a number of aryl diazonium chlorides. The properties of these compounds and their analytical data are recorded in Table II.

TABLE II

Diazonium chloride of amines.	Colour in acetic acid.	M.P.	% Sulphur. Found.	Calc.
Aniline	Dirty yellow	167°	8.65	8.60
o-Toluidine	Pale yellow	170°	8.34	8.29
p-Toluidine	Yellow	157°	8.38	8.29
α-Naphthylamine	Brown	138°	7.52	7 58
β-Naphthylamine	Scarlet-red	143°	7.63	7.58
Sulphanilamide	Bright yellow	153°	14.23	14.19

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SYNTHESIS IN ACRIDINE SERIES. PART IV. 5-N-SUBSTITUTED 2 : 4-DIBROMO- AND 2 : 4-DIBROMO-7-METHOXYACRIDINE

By G. S. Patel, S. R. Patel and K. S. Nargund

5-N-substituted amino-2 : 4-dibromo-7-methoxy and the corresponding demethoxy-acridine derivatives have been described.

Work described in the present communication is in connection with the synthesis of 5-N-substituted 2 : 4-dibromo-(I) and 2 : 4-dibromo-7-methoxy-acridine (II) derivatives and these have been obtained by the well-known method (Drozdov, *J. Gen. Chem.*, 1938, **8**, 937 ; Goodall and Kermack, *J. Chem. Soc.*, 1936, 1546) consisting of the cyclisation of the amide of the corresponding diphenylamine-2-carboxylic acid obtained from the acid chloride of the latter and the necessary amine.

3′ : 5′-Dibromo-(III) and 3′ : 5′-dibromo-4-methoxydiphenylamine-2-carboxylic acids (IV), required for the synthesis of (I) and (II), were obtained by Ullmann's condensation of 3 : 5-dibromoaniline respectively with *o*-chlorobenzoic acid and 2-bromo-5-methoxybenzoic acid. Compounds (III) and (IV) on cyclisation with excess of phosphorus oxychloride afforded 2 : 4-dibromo- and 2 : 4-dibromo-7-methoxyacridone respectively, instead of the expected 5-chloroacridine derivatives. Hence, the facile method of obtaining 5-N-substituted acridine derivatives by allowing the corresponding 5-chloroacridine to react with an amine in presence of phenol is not applicable for the synthesis of (I) and (II), described here.

Experimental

3′:5′-Dibromo-4-methoxydiphenylamine-2-carboxylic Acid (IV).—A mixture of 2-bromo-5-methoxybenzoic acid (10 g.), 3 : 5-dibromoaniline (13 g.), fused potassium carbonate (8 g.), *iso*amyl alcohol (50 c.c.) and a trace of copper powder was refluxed for 3 hours at 130-35°. *iso*Amyl alcohol was removed by steam-distillation and the resulting solution after treatment with charcoal was filtered, acidified, and the product was collected and washed with boiling water. It crystallised from glacial acetic acid in small plates, m.p. 205-207°, yield 15 g. (Found : Equiv., 395.0 ; Br, 40.6. $C_{14}H_{11}O_3NBr_2$ requires equiv., 401.0 ; Br, 39.9%).

The *acid chloride* was obtained by refluxing a mixture of the above acid (1 g.), thionyl chioride (3 c.c.) and benzene (10 c.c.) and crystallised from benzene-petrol as brown needles, m.p. 161-63°. (Found : Cl, 8.5 ; Br, 38.7. $C_{14}H_{10}O_2NClBr_2$ requires Cl, 8.4 ; Br, 38.1%).

Formation of 2 : 4-Dibromo-7-methoxyacridone.—The above acid (1 g.) and $POCl_3$ (4 c.c.) were heated at 105-110° for 1 hour and the excess of oxychloride was removed by distillation under reduced pressure. The residual liquid was decomposed by pouring it over a mixture of ice and ammonia solution, and the product obtained was filtered immediately, washed with a large amount of water and allowed to dry in air.

It was insoluble in benzene and chloroform. It crystallised from boiling glacial acetic acid in yellow powder, m.p. > 300°, yield 0.6 g. (Found : Br, 41.1. $C_{14}H_{19}O_2NBr_2$ requires Br, 41.7%).

5′ : 5′-Dibromodiphenylamine-2-carboxylic acid (III) was obtained by the Ullmann condensation of *o*-chlorobenzoic acid with 3 : 5-dibromoauniline. It crystallised from acetic acid as a greenish yellow powder, m.p. 247-49°. (Found : Equiv., 365.0; Br, 43.5. $C_{13}H_9O_2NBr_2$ requires equiv., 371.0 ; Br, 43.1%).

The *acid chloride* crystallised from petroleum ether as a yellow powder, m.p. 118-20°. (Found : Cl, 9.2; Br, 41.5. $C_{13}H_8ONClBr_2$ requires ; Cl, 9.1 Br, 41.1%).

Formation of 2 : 4-Dibromoacridone.—The reaction was carried out as described above under compound (IV) with $POCl_3$. The product obtained crystallised from glacial acetic acid as a yellowish light powder, m.p. > 300°. (Found : Br, 46.1. $C_{13}H_7ONBr_2$ requires Br, 45.3%).

2 : 4-Dibromo-5-(δ-diethylamino-α-methylbutyl)-aminoacridine (I) *Dihydrochloride.*—To a solution of the chloride of (IV) (0.01 *M*) in minimum quantity of benzene δ-diethylamino-α-methylbutylamine (0.011 *M*) was added and the mixture was refluxed on a water-bath for half an hour. Excess of benzene was removed by distillation at 110° and to the residue $POCl_3$ (25 c.c.) was added, and heating was continued at 110° for 2 hours. Excess of $POCl_3$ was removed by distillation under reduced pressure and the cold residual thick liquid was dissolved in a minimum amount of absolute alcohol. The alcoholic extract was filtered and diluted with excess of acetone till the solution became highly turbid, and kept overnight. The yellow solid separating was collected and crystallised from alcohol-acetone mixture as a yellow powder, m.p. 222-26° (decomp.). (Found : Cl, 12.2 ; Br, 27.3. $C_{23}H_{31}ON_3Cl_2Br_2$ requires Cl, 11.9; Br, 26.8%).

Other 5-N-substituted aminoacridine derivatives have been obtained by following the method described above and are recorded in Table I.

TABLE I

Hydrochloride of 2 : 4-dibromo-5-substituted acridines.	M.P.*	Found		Mol. formula.	Calc.	
		Br.	Cl.		Br.	Cl.
-5-(γ-piperidino-propyl)-amino-7-methoxy-	250-52°	27.9 %	12.5%	$C_{22}H_{27}ON_3Cl_2Br_2$	27.6%	12.2%
-5-(δ-diethylamino-α-methyl-butyl)-amino-	218-20°	28.7	12.7	$C_{22}H_{29}N_3Cl_2Br_2$	28.2	12.5
-5-(γ-piperidino-propyl)-amino-	237-40°	29.4	13.1	$C_{21}H_{25}N_3Cl_2Br_2$	29.0	12.9

* With decomposition

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MODIFIED IODOMETRIC METHOD FOR THE ESTIMATION OF ZINC

By R. K. Nanda and B. Prasad

Zinc can be estimated iodometrically with the help of potassium ferricyanide and potassium iodide in acetate-acetic acid buffer medium if p_H of the solution is maintained between 3 and 4. The excess ferricyanide concentration in solution should not exceed 2-m*M*/litre.

The iodometric method for the estimation of zinc was first used by Lang (*Z. anal. Chem.*, 1929, **79**, 161) in a slightly acidic solution, adding small amounts of ferricyanide at a time. The results were about 1.65% lower than the stoichiometric value. Maun and Swift (*Anal. Chem.*, 1949, **21**, 798) added the ferricyanide in one lot and adjusted the p_H of the medium between 2 and 3 with phthalate buffer. They could estimate a minimum of 65 mg. of zinc accurately. Their stoichiometrically calculated values had to be multiplied by 1.019 to provide correct values. A large excess of ferricyanide, however, afforded higher results, particularly with smaller amounts of zinc. In the present work, the effects of p_H and the excess ferricyanide concentration have been studied with acetate-acetic acid buffer medium.

Experimental

Reagent grade chemicals were always used. The stock solution of approximately 0.1*M* sodium thiosulphate was standardised against potassium iodate from time to time. Approximately 0.1*M* solution of potassium ferricyanide was prepared in cold distilled water and was kept in dark when not in use. Anhydrous zinc sulphate was prepared by heating 'Analar' quality hydrated zinc sulphate to 300° ± 5°. Solutions of zinc sulphate were made by weight from this sample. The strength was also checked by precipitating and weighing as zinc ammonium phosphate.

In order to study the effect of the excess of ferricyanide on iodide in the acetate-acetic acid medium, several experiments (without zinc) were performed at p_H 3, 4 and 5 approximately, taking different amounts of ferricyanide, while keeping the iodide concentration and the total volume of the solution the same. Iodine liberated after 10 minutes in dark was estimated. When the p_H of the solution was approximately between 3 and 4 and the ferricyanide added did not exceed 2 m*M* per litre, no iodine was found to be liberated within 10 minutes.

The actual method employed for the estimation of zinc is shown below. The results obtained with different amounts of zinc, both at p_H 3 and 4, are shown in Table I, from which the amount of zinc found appears to be always less than the amount taken. The plot of the amount of zinc, found by calculation, against the amount taken, gave a straight line in each set of experiments. From the plots the average multiplication factor came out to be 1.020. A minimum of 30 mg. of zinc could be estimated by this method. It may be mentioned that the addition of ammonium sulphate rapidly coagulates the precipitate, rendering a sharper end-point. If p_H exceeds 4, the end-point becomes unstable.

TABLE I

Expt. No.	p_H of the soln.	Ferricyanide added.	Ferricyanide in excess.	Thiosulphate required (m.e.).	*Zn found.	**Zinc found.	Zn taken.
I (a)	(4±0.2) approx.	4.3 c.c.	1.0 c.c.	0.3016	0.02956 g.	0.03015 g.	0.03016 g.
(b)	,,	7.6	,,	0.6034	0.0591	0.06029	0.06032
(c)	,,	17.5	,,	1.508	0.1478	0.1508	0.1508
II (a)	(4±0.2) approx.	8.3	5.0	0.3027	0.0296	0.03026	0.03016
(b)	,,	11.5	,,	0.6043	0.0592	0.06040	0.06032
(c)	,,	18.0	,,	1.205	0.1181	0.1205	0.1206
(d)	,,	21.5	,,	1.508	0.1478	0.1508	0.1508
III (a)	(3±0.2) approx,	4.3	1.0	0.3016	0.0295	0.03015	0.03016
(b)	,,	7.6	,,	0.6034	0.0591	0.06029	0.06032
(c)	,,	17.5	,,	1.508	0.1478	0.1508	0.1508
IV (a)	(3±0.2) approx.	8.5	5.0	0.3260	0.0319	0.03296	0.03246
(b)	,,	12.5	,,	0.6463	0.0638	0.06510	0.06492
(c)	,,	23.0	,,	1.620	0.1589	0.1621	0.1623

* Stoichiometrically.

** Using the multiplying factor.

Measured volumes of zinc sulphate solution containing different amounts of zinc along with KI (3 g.), ammonium sulphate (5-10 g.) and 50 c.c. of approximately molar ammonium acetate were taken in 500 c.c. stoppered bottles. About 45 c.c. of N-H_2SO_4 (to adjust the p_H between 3 and 4) and necessary amount of water to make the volume up to about 250 c.c. were added. A calculated amount of potassium ferricyanide ($\sim 0.1M$) solution (depending upon the amount of zinc present in solution ; cf. Table I) was added in one lot, such that the excess ferricyanide concentration in solution did not exceed 2 millimoles per litre. (When the zinc content of the solution is unknown, a rough experiment may be performed with sufficiently large excess of ferricyanide). The mixture was swirled and kept in dark for 5 minutes. It was then taken out and titrated against a standard thiosulphate solution to the conventional starch iodide end-point. The amount of zinc calculated stoichiometrically multiplied by the factor 1.020 gives the actual amount of zinc in solution.

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DIAQUO-MONO-OXALATO-ANTIMONY COMPLEX

By Ch. B. N. Nanda and S. Pani

Aquo-hydroxo-mono-oxalato-antimony complex (A), which loses the molecule of water at 110° to 120°, but not over sulphuric acid, has been prepared. From the solubility of this complex at 35° in partially neutralised oxalic acid solution of various concentrations and p_H, the above complex has been found to react with a hydrogen ion, furnishing Sb^{+}, which further reacts with an oxalate ion affording dioxalato-antimonite complex. The equilibrium constants of both the reactions have been determined.

Oxalate ion has been found to be removed to the solid phase when antimony oxide is kept in contact with a solution of less than 50% neutralised oxalic acid. This phenomenon is not observed with a solution containing more than 50% neutralised oxalic acid (Nanda and Pani, this *Journal*, 1954, **31**, 588). The system at lower p_H containing less than 50% neutralised oxalic acid has been investigated. The removal of oxalate from the solution to the solid phase is a clear indication of the formation of an insoluble oxalate compound of antimony. The amount of oxalate removed from the solution depends on the p_H of the solution, but the amount of antimony oxide added being indefinite, the solid phase has no stoichiometric composition. The composition of the solid phase therefore varies with the solid antimony oxide added. It becomes thus difficult to study the system containing two solid phases in equilibrium with the solution. It was therefore thought proper to prepare the insoluble compound first and study its properties.

Experimental

The chemicals used were of Analar quality. Freshly prepared antimony oxide was refluxed with a concentrated solution of oxalic acid. The crystalline substance obtained was filtered, washed and dried at 110-20°. It was analysed for antimony content by standard potassium bromate, and antimony together with oxalate content, by standard potassium permanganate. The compound contains 53.59% Sb and 38.75% oxalate [calc. 53.69% and 38.82% respectively for $[Sb(OH)C_2O_4]$. The same compound is also obtained by treating a solution of tartar emetic with a solution of oxalic acid. A hydrated compound

$$\left[Sb\begin{cases} C_2O_4 \\ OH \\ OH_2 \end{cases} \right]$$

containing one molecule of water of crystallisation was obtained by dissolving a small amount of oxalic acid in a saturated aqueous solution of antimony chloride and heating gently to remove HCl. The compound was precipitated by adding ether in which antimony chloride and even saturated aqueous solution of antimony chloride were soluble. The compound was washed with ether and dried over H_2SO_4 in vacuum. It is free from chloride and contains 49.83% Sb and 35.89% $C_2O_4^{2-}$ (calc. 49.74% and 35.96% respectively for $SbOH.C_2O_4, H_2O$). The same compound can also be obtained by the first two methods provided that the samples are dried over H_2SO_4 and not at 110° to 120°. The water molecule most probably is present in the co-ordination sphere

and the compound is mono-aquo-monohydroxo-mono-oxalato-antimony complex. In a number of antimony complexes studied here, the co-ordination number of the antimony has been reported to be 4.

Several four-co-ordination solid antimony complexes have also been prepared (unpublished). It has been reported that the co-ordination num ber of antimony ($CsSb_2F_7$) is 4 (Bystrom and Wilhelmi, *Arkiv Kemi*, 1951, **3**, 373).

All these are in favour of the assumption that the $Sb.OH.C_2O_4$, H_2O is a four-co-ordination complex. The compound is almost insoluble in water, but is slowly hydrolysed to antimony oxide and oxalic acid. The solubility in oxalic acid is also very smally, but the solubility increases in partially neutralised oxalic acid. The compound was added to a 25% neutralised oxalic acid of known concentration and shaken in an electric shaker ; when the equilibrium was reached, the oxalate content and antimony content were determined as before. It was found that the increase in oxalate content in g. moles in the solution was equal to the g. atoms of antimony in the solution. It is therefore concluded that the compound is not hydrolysed in oxalate solution and the solid phase, remaining in equilibrium with partially neutralised oxalic acid, is hydrated antimonyl oxalate, $HO.Sb.C_2O_4.H_2O$.

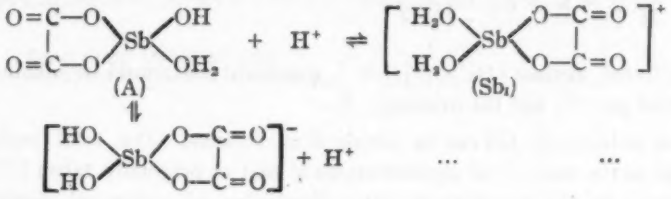
The solubility of antimonyl oxalate in partially neutralised oxalic acid solution of various concentrations at 35° and the p_H are recorded in Table I. The concentrations are expressed as [X] which indicates g. moles of X per litre.

TABLE I

Neutralisation.	[OX].	p_H.	[Sb]$\times 10^3$.	[$HC_2O_4^-$].	[Sb_I]$\times 10^4$.	[Sb_{II}]$\times 10^3$.	$K_1 \times 10^2$.
	0.2708	1.40	3.21	0.1581			
	0.2407	1.42	2.93	0.1427			
10%	0.2106	1.44	2.66	0.1270			
	0.1854	1.48	2.38	0.1162			
	0.1505	1.53	2.11	0.09797			
	0.1204	1.59	1.82	0.08175			
	0.2708	1.50	4.53	0.1716	5.218	4.008	2.34
	0.2407	1.64	3.77	0.1692	3.780	3.391	2.01
20%	0.2106	1.67	3.35	0.1481	3.528	2.997	2.02
	0.1854	2.76	3.03	0.1401	2.867	2.743	1.96
	0.1505	1.82	2.81	0.1168	2.498	2.570	2.20
	0.1204	1.92	2.24	0.09699	2.077	2.032	2.10
	0.2708	1.55	5.99	0.1775	4.650	5.525	3.11
	0.2407	1.65	5.03	0.1693	3.694	4.661	2.74
30%	0.2106	1.68	4.51	0.1521	3.447	4.165	2.73
	0.1854	1.77	3.89	0.1401	2.852	3.608	2.58
	0.1505	1.88	3.17	0.1188	2.278	2.942	2.48
	0.1204	1.96	2.57	0.0990	1.809	2.389	2.41
	0.2708	2.06	10.28	0.2261	1.4370	10.140	4.48
	0.2407	2.10	8.98	0.2035	1.3110	8.849	4.35
0%	0.2106	2.23	7.48	0.1843	0.9716	7.383	4.00
	0.1854	2.29	5.81	0.1649	0.8463	5.725	3.64
	0.1505	2.40	4.66	0.1362	0.6569	4.594	3.37
	0.1204	2.53	3.77	0.1109	0.4870	3.721	3.35

At the first sight the results appear to indicate that the solubility increases with increasing p_H (increasing neutralisation of oxalic acid). The results of each set, however, indicate that the maximum solubility in that set is observed in the solution in which the p_H is maximum. The solubility is therefore controlled by two factors, namely, hydrogen ion and oxalate ion.

Antimonyl oxalate is formed when antimony oxide is in contact with oxalic acid solution ; a species of antimonyl oxalate (containing one oxalate per atom of antimony) evidently exists in solution. The soluble species, however, cannot be $Sb.OH.C_2O_4, H_2O$ since the increase in its solubility with increasing concentration of oxalate ion cannot be explained. The antimonyl oxalate therefore goes into solution either as a cationic (equation 1) or anionic complex (equation 2).



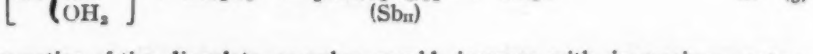
... (1)

... (2)

Hydrated antimony oxalate is therefore very similar to antimonious acid and the reactions (1) and (2) are very similar to the basic and acidic dissociation of antimonious acid (hydrated antimony oxide), as proposed in an earlier communication (Nanda and Pani, this *Journal*, 1955, **32**, 525).

If reaction (1) is assumed to be taking place, the concentration of the mono-oxalato cationic complex would be small at higher p_H.

If reaction (2) is assumed to be taking place, the concentration of the anionic complex in solutton would increase with p_H, and in 50% or more neutralised oxalic acid solution, a significant amount of antimony would exist as anionic mono-oxalato complex. This is, however, not observed. The complex in such medium is dioxalato complex. It is therefore very probable that mono-oxalato complex, if at all exists, would be the cationic rather than the anionic one. The other reaction taking place would be the formation of the dioxalato complex by the interaction of the antimonyl oxalate with bioxalate ion.



... (3)

The formation of the dioxalato complex would increase with increasing neutralisation of oxalic acid. The equilibrium constants of the reactions (1) and (3) are given by equation (1-1) and (3-1) respectively.

$$\frac{[Sb_I]}{[H^+]} = K \qquad \ldots \quad (1\text{-}1)$$

$$\frac{[Sb_{II}]}{[HC_2O_4^-]} = K_1 \qquad (3\text{-}1)$$

$[Sb_I]$, $[Sb_{II}]$, $[H^+]$ and $[HC_2O_4^-]$ represent respectively the molar concentration of the mono-oxalato cationic complex, dioxalato complex, hydrogen ion and bioxalate ion. Since both the reactions would take place, it is difficult to calculate K and K_1. It can, however, be calculated as follows. Let [Sb] be the total antimony in the solution. Hence,

$$[Sb] = [Sb_I] + [Sb_{II}] \qquad \ldots (4)$$

Substituting the value of $[Sb_I]$ from equation (1-1) and that of $[Sb_{II}]$ from equation (3-1) in equation (4), one gets

$$[Sb] = K[H^+] + K_1[HC_2O_4^-]$$

or

$$\frac{[Sb]}{H^+} = K + K_1 \cdot \frac{[HC_2O_4^-]}{[H^+]} \qquad \ldots (4\text{-}1)$$

If $[Sb]/[H^+]$ is plotted against $[HC_2O_4^-]/[H^+]$, a straight line would be obtained, the slope of which would give K_1 and the intercept, K.

The concentration of bioxalate ion can be obtained as follows. The total oxalate in the solution is equal to the sum of the concentrations of that of originally taken [OX] and the oxalate brought to the solution due the dissolution of antimonyl oxalate. Total oxalate = [OX] + [Sb]. Total oxalate in the solution is partly present in mono-oxalato complex Sb_I, partly in dioxalato complex Sb_{II}, and the rest as free oxalic acid, bioxalate ion and oxalate ion. Hence,

$$[OX] + [Sb] = [Sb_I] + 2[Sb_{II}] + [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] \qquad \ldots (5)$$

Since $[Sb_I] + [Sb_{II}] = [Sb]$,

$$[OX] - [Sb_{II}] = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$$

$$= [HC_2O_4^-]\ \frac{[H^+]}{k_1} + [HC_2O_4^-] + \frac{k_2}{[H^+]} \cdot [HC_2O_4^-]$$

where k_1 and k_2 are respectively the first and the second dissociation constant of oxalic acid ($k_1 = 5.7 \times 10^{-2}$, $k_2 = 6.9 \times 10^{-5}$; *Z. physikal. Chem.*, 1920, **86**, 381).

$$[HC_2O_4^-] = \frac{[OX] - [Sb_{II}]}{\frac{[H^+]}{k_1} + 1 + \frac{k_2}{[H^+]}} = \frac{[OX] - [Sb_{II}]}{a} \qquad \ldots (5\text{-}1)$$

The concentration of bioxalate ion can be calculated if $[Sb_{II}]$ is known. When the concentration of Sb_{II} is very small and most of the antimony exists as Sb_I,

$$[HC_2O_4^-]_1 = \frac{[OX]}{a} \qquad \ldots (5\text{-}2)$$

When the concentration of Sb_I is very small and most of the complex is dioxalato complex Sb_{II},

$$[HC_2O_4^-]_2 = \frac{[OX] - [Sb]}{a} \qquad \ldots (5\text{-}3)$$

$[HC_2O_4^-]_1$ and $[H\,C_2O_4^-]_2$ for the 10% neutralised series were calculated. Since [Sb] is small compared to [OX] in this series, the difference between $[HC_2O_4^-]_1$ and $[HC_2O_4^-]_2$ is very small. The actual concentration of $HC_2O_4^-$ would not be much different from these values. Assuming $[HC_2O_4^-]_2$ to be very nearly equal to $[HC_2O_4^-]$, $[Sb]/[H^+]$ was plotted against the corresponding $[HC_2O_4^-]/[H^+]$. Very nearly a straight line was obtained (out of six points four were on the straight line and two deviated a little). The value of K obtained from the intercept is 1.65×10^{-2}. Using this value of K, the concentration of Sb_I was calculated by equation $(1-1)$. $[Sb_{II}]$ was obtained by subtracting $[Sb_I]$ from [Sb]. The concentration of bioxalate ion was calculated by equation (5-1). The value K_1 calculated are shown in Table I. The mean value is 2.88×10^{-2}. The value of K_1 obtained from the slope of the straight line obtained with 10% neutralised series is 1.6×10^{-2} is not much different from the above mean value.

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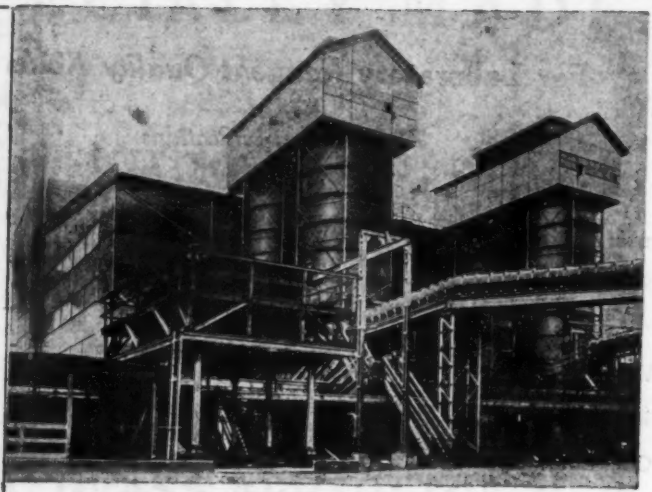

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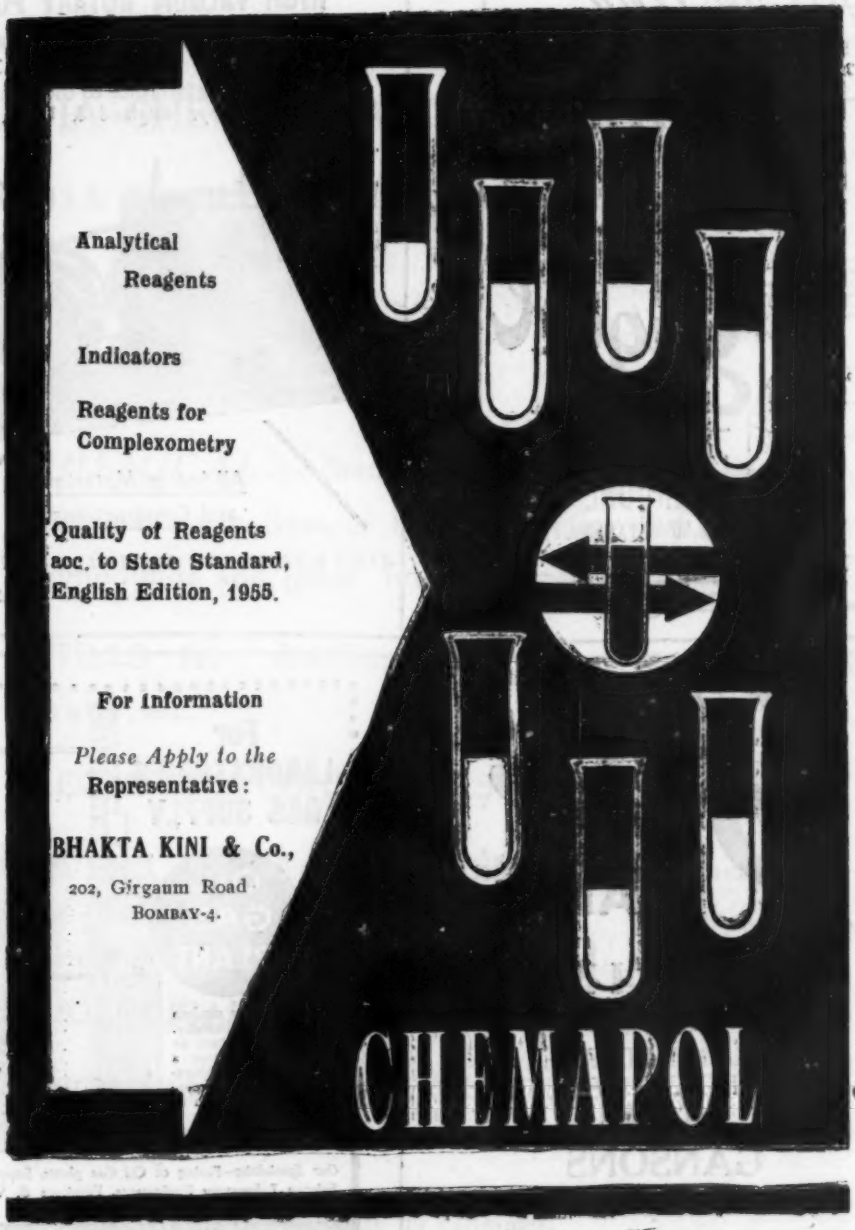

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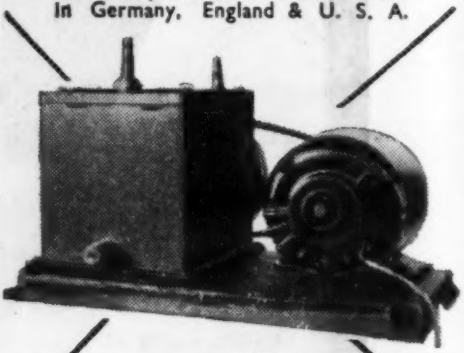

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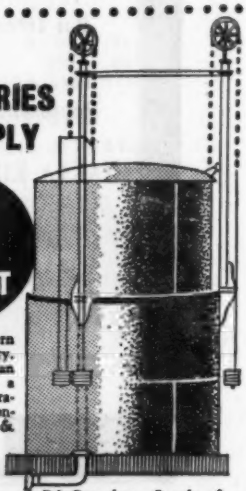

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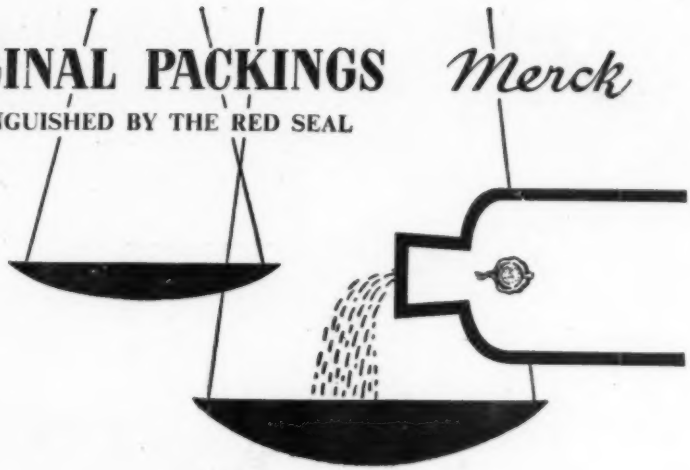

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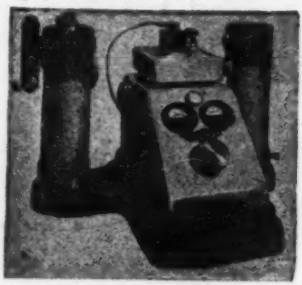

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